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**Transactions of the Faraday Society**



# **Transactions of the Faraday Society.**

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**FOUNDED 1903**

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**TO PROMOTE THE STUDY OF ELECTROCHEMISTRY, ELECTROMETALLURGY,  
PHYSICAL CHEMISTRY, METALLOGRAPHY, AND KINDRED SUBJECTS.**

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**VOL. XXIV. 1928**

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**GURNEY AND JACKSON  
LONDON: 33 PATERNOSTER ROW  
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**The General Discussion on the above papers will be reported in No. 91, to be published on, or shortly after, 1st December, 1928.**

## **THE PHYSICAL SOCIETY AND THE OPTICAL SOCIETY: THE NINETEENTH ANNUAL EXHIBITION OF Electrical, Optical, and other Physical Apparatus is to be held by the Physical Society and the Optical Society on 8th, 9th and 10th JANUARY, 1929 At the Imperial College of Science and Technology, South Kensington.**

As on previous occasions the Exhibition will be divided into a Trade Section, comprising the exhibits of manufacturing firms, and a Research and Experimental Section. The Exhibition Committee invites offers, from Research Laboratories and Institutions and from individual research workers, of exhibits suitable for inclusion in the Research and Experimental Section. The exhibits in this section will be arranged in three groups:—

- (a) Exhibits illustrating the results of recent physical research.
- (b) Lecture Experiments in Physics.
- (c) Historical exhibits in Physics.

Accommodation for these exhibits will be provided in rooms separate from those devoted to the trade exhibits; and a part of the Catalogue will be devoted to their description. No charge will be made for space or catalogue entries in the Research and Experimental Section, and the facilities of the Imperial College will be at the disposal of the exhibitors.

Offers of exhibits for inclusion in any of the above three groups should be communicated immediately, and in any case **not later than November 14th**, to the Secretary, Physical and Optical Societies, 1 Lowther Gardens, Exhibition Road, London, S.W. 7. Brief particulars of space and other facilities required should be given.

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# THE ELECTRONIC THEORY OF VALENCY, PART VI, THE MOLECULAR STRUCTURE OF STRONG AND WEAK ELECTROLYTES. (b) REVERSIBLE ION- ISATION.

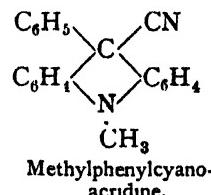
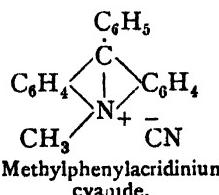
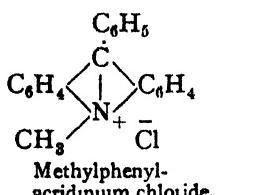
BY T. MARTIN LOWRY.

*Received 4th April, 1927.*

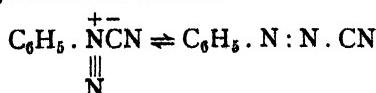
The theory of complete ionisation has met with such marked success that it might easily be supposed that it could be applied to all electrolytes. The present paper therefore contains a review of those cases in which the ionisation of an electrolyte is reversible instead of complete.

## True Electrolytes and Pseudo-electrolytes.

The most obvious examples of reversible ionisation are provided by those compounds in which neutralisation of the opposite charges of the ions is rendered possible by a change of molecular structure. Thus, according to the electronic theory of valency, a substituted ammonium chloride must remain permanently ionised, since both the ammonium ions and the chloride ions carry complete shells of electrons and cannot share electrons without creating a surplus. There are, however, a number of cases in which this surplus can be disposed of by a rearrangement of bonds within the molecule, giving rise to a wholly covalent compound. This change takes place with greater readiness when the chlorine is replaced by an anion of a less strongly negative character, *i.e.*, by a radical which is less hungry for electrons and therefore more ready to share them with another atom. Thus methylphenylacridinium chloride is a true electrolyte, which remains permanently ionised in aqueous solutions; but, when sodium cyanide is added, a progressive fixation of cyanogen ions takes place, until after about a day at 25°, the conductivity is found to have fallen almost to the value for sodium chloride, as a result of the complete conversion of the ionised "true salt" into an insoluble "pseudo-salt."<sup>1</sup>



A similar change of structure can be effected in the diazocyanides by separating the "salt" from aqueous solutions and dissolving it in a non-ionising solvent, when it behaves as a typical non-electrolyte, whereas in water it behaves just like the chloride

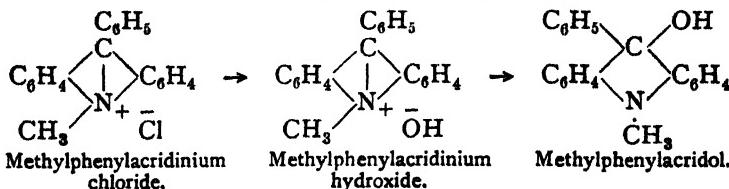


Diazonium cyanide.      Diazo-cyanide.

<sup>1</sup> Hantzsch and Kalb, *Ber.*, 1899, 32, 3109

## ELECTRONIC THEORY OF VALENCY

Precisely similar considerations apply to the fixation of a hydroxyl-ion. Thus a solution of methylphenylacridinium chloride, when mixed with an equivalent quantity of sodium hydroxide, shows at first the normal conductivity of such a mixture; but this conductivity diminishes progressively to that of sodium chloride as the hydroxyl is "fixed" by the anion.



In the same way, the conductivity of a mixture of the sulphate with the calculated quantity of baryta gave a conductivity which decreased in the course of 900 minutes from 119·2 to 1·7 Siemens' units, as a result of the "fixation" of the hydroxyl ions of the "true base" to an isomeric form of its kation, with the formation of an isomeric "pseudo-base."<sup>2</sup> The acridol, which is formed as a product, is a tertiary amine-alcohol, compare  $(C_6H_5)_2NMe$  and  $(C_6H_5)_3C \cdot OH$ . It is therefore just as true a base as trimethylamine, but differs from other tertiary bases in that one of the alkyl radicals carries a hydroxyl-group, which is eliminated in the form of water as soon as the base has performed its characteristic function of accepting a proton from an acid. Although, therefore, it is commonly referred to as a "pseudo-base," it would perhaps be described more accurately as a "pseudo-alkali," i.e., as a non-electrolytic isomer of a quaternary ammonium hydroxide.

It is probably a mistake to think of these pseudo-electrolytes as if they were non-electrolytes *per se*. If this were the case, it would be impossible to reconvert a "pseudo-base" such as methylphenylacridol into the corresponding acridinium chloride, except by a process analogous to the esterification of an alcohol. It is therefore probably correct to think of them as "weak electrolytes,"<sup>3</sup> just like any other compound which can exist both in an ionised and in a covalent form; but, whereas the strongly negative radicals, such as chlorine, are ionised readily (liberating a trace of the acridol ion which reverts at once to the more stable isomeric acridinium ion), the ionisation of the less strongly negative radicals, such as hydroxyl and cyanogen, is so small that the equilibrium is displaced almost completely in the direction of the pseudo-electrolyte.<sup>3</sup> This conclusion is even more obvious in the case of the "pseudo-acids" referred to below, where the reversibility of the prototropic change<sup>4</sup> depends on the presence of a mobile hydrogen atom in *both* of the isomeric hydrides.

### Strong and Weak Acids.

Whilst the conception of a "strong electrolyte" is a very modern one, the existence of strong and weak acids has been familiar for 1000 years or more, and had already been interpreted in many other ways before the strength of an acid was finally correlated with its electrical conductivity in dilute solutions. The theory of complete ionisation therefore receives its most serious challenge from the existence of weak acids, which obey Ostwald's dilution law ( $a \propto c^{-1}$ , where  $a$  is small), and cannot therefore

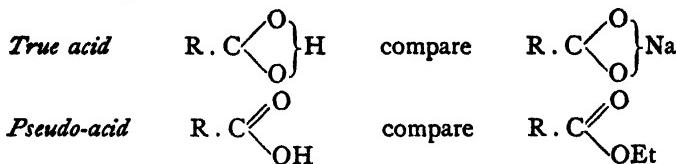
<sup>2</sup> Hantzsch and Kalb, *Ber.*, 1899, 32, 3109.

<sup>3</sup> Flürsheim, *J. Chem. Soc.*, 1910, 97, 90-94.

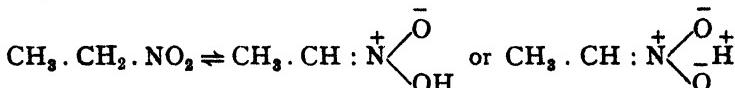
<sup>4</sup> *J. Chem. Soc.*, 1923, 123, 828.

also obey the dilution formula for strong electrolytes ( $I = a c \sigma^{\frac{1}{2}}$ , where  $a$  is large).

In order to account for the existence of these weak acids, Hantzsch has suggested<sup>5</sup> that carboxylic acids can exist in two interconvertible isomeric forms, thus:

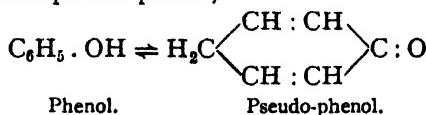


A dynamic isomerism of this type is actually observed in the nitro-paraffins.

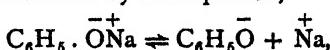


and is an obvious factor in reducing the acidity of the compound, since this must be diminished in direct proportion to the extent to which the true acid is converted into the isomeric pseudo-acid. The correctness of this theoretical view has been established by Hantzsch's observations on the *gradual loss* of conductivity which takes place when the true acid, freshly liberated from its salts, changes slowly into the isomeric pseudo-acid (of which the conductivity is usually so small as to be negligible), and by the *gradual decrease* of conductivity which occurs when a pseudo-acid is neutralised by an alkali.

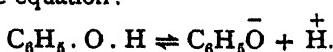
It is, however, by no means certain that the contrast between strong and weak acids depends in other cases on so definite a phenomenon. For instance, we need not suppose that phenol owes its weak acidity to conversion into an isomeric pseudo-phenol.



since it is sufficient to postulate that, whilst the  $- \ddot{\text{O}}\text{Na}$  radical of sodium phenate is permanently ionised, the  $- \text{OH}$  radical of phenol is held together by a real bond, just as in the case of the alcohols. Dissolution of the sodium compound in water would then give rise to a direct dissociation of ready-made ions as indicated by the equation,



whereas, in the case of phenol itself, ions could only be produced as the result of a destruction of neutral molecules, by the rupture of the hydrogen-oxygen bond, as in the equation:



Some care is needed in order to formulate these views in accordance with modern theories of atomic structure, since, as pointed out in an article on "The Uniqueness of Hydrogen"<sup>6</sup> exceptional difficulty is experienced in deciding whether an atom of hydrogen is linked to the rest of the molecule by a real bond or by a mere electrovalence. This difficulty arises from

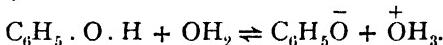
<sup>5</sup> *Ber.*, 1917, 50, 1438.

<sup>6</sup> Lowry, *Chemistry and Industry*, 1933, 42, 43.

the fact that, since the hydrogen "shell" contains 0 or 2 instead of 8 electrons, the ordinary static symbolism makes no distinction between these two forms of union. Thus, in the case of  $\text{H}:\ddot{\text{Cl}}:$ , the same electronic

formula serves equally well to represent a pair of ions,  $\text{HCl}$ , with 0 and  $2 + 8 + 8$  electrons, or a covalent compound,  $\text{H} - \text{Cl}$ , in which 2 of the 18 electrons are shared by the two atoms. When, however, a dynamic model is used, and shared electrons are regarded as moving in binuclear orbits, a clear distinction between the two types of union again becomes possible, according as the orbits of the electrons in question surround two nuclei or only one. If this distinction is admitted, it appears probable that hydrogen is covalent in all its compounds, and that the free hydrogen ion

or naked proton represented by the symbol  $\text{H}^+$  does not exist except as a transient product in a vacuum-tube or the like. This conclusion follows, on the one hand, from the fact that there are no electrostatic forces to prevent such a nucleus from falling inside the electronic orbits of any other atom with which it may collide, and, on the other hand, from numerical data which show that the union of a proton with water to form a hydrated hydrogen ion would liberate not less than 260,000 calories.<sup>7</sup> The ionisation of an acid (which does not take place when the pure compound is merely melted) must then be formulated as depending on an interaction of the acidic hydride with water, or the like, giving rise to an oxonium ion, as in the equation,

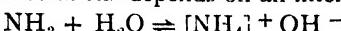


It will be seen, however, that this scheme still possesses the characteristic which is now put forward as an essential feature of all "weak" electrolytes, that the opposite electric charges of the ions can be neutralised without any violation of the "octet" rule, giving rise to products in which the electro-valence of the ions is replaced by a real bond.

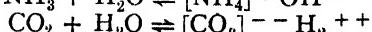
### Strong and Weak Bases.

Bases resemble acids in exhibiting a very wide range of strengths. Thus the soluble metallic hydroxides (which include the alkalis) are all strong bases, and their strength is shared by the quaternary ammonium hydroxides, where the formation of a covalent bond between nitrogen and oxygen is prevented by the fact that the nitrogen is unable to attach itself by real bonds to five atoms simultaneously. Weak bases appear to be of two main types, since covalent compounds can be formed, either by fixing the hydroxyl-group by a real bond to an isomeric form of the cation, as in the acridinium compounds cited above, or by eliminating it in the form of a covalent molecule of water. The latter case is extremely common. Thus the amines generally behave as weak bases, since the concentration of hydroxyl-ions in their solutions depends on an interaction with water:

e.g.,



compare



the ready reversibility of which is shown by the complete removal of ammonia from its aqueous solutions by boiling, or of aniline by steam-distillation. Since, however, this dehydration has the effect of eliminating the unbalanced electric charges from the system, giving rise exclusively to covalent compounds, this explanation is in close agreement with the general

<sup>7</sup> Fajans, *Ber. deut. physik. Ges.*, 1919, 21, 709.

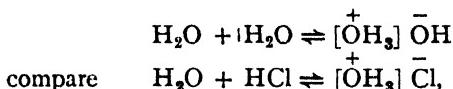
proposition set out above as regards the essential characteristics of a weak electrolyte.

The problem of weak bases has, however, been carried one stage further by Latimer and Rodebush,<sup>8</sup> who have suggested that the hydrate  $\text{NH}_3 \cdot \text{H}_2\text{O}$

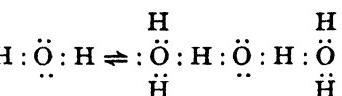
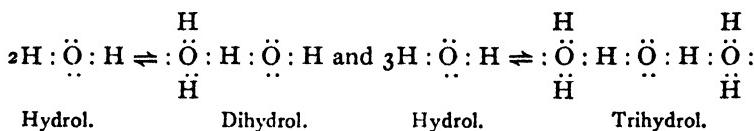
may be formulated as  $\text{H} : \ddot{\text{N}} : \text{H} : \text{O} : \text{H}$ . This formula represents the monohydrate as a covalent isomer of ammonium hydroxide,



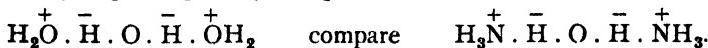
in which the hydroxyl radical is united to the ammonium radical by a real bond, as required by our definition of a weak electrolyte. The fulfilment of this condition is not vitiated by the fact that, since quadrivalent nitrogen is always positively-charged, and bivalent hydrogen is negatively-charged, the resulting molecule would exhibit the phenomenon which J. J. Thomson has described as "intramolecular ionisation."<sup>9</sup> The bivalence of hydrogen is also of value in accounting for the fact that the polymerisation of liquid water is not accompanied by ionisation. Thus, if hydrogen were always univalent, the formation of a double-molecule would be represented by the scheme,



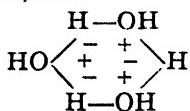
and the product would be an oxonium hydroxide, just like ammonium hydroxide; but, if the hydrogen is bivalent, the formation of double and triple molecules can be represented, *without any formation of free ions*, by the schemes,



Here again the polymerised molecules must exhibit "intramolecular ionisation," since the tervalent oxonium oxygen is positively-charged, and the bivalent hydrogen negatively-charged, as in the formula,



Alternatively the trihydrol can be represented by a ring structure dissected from the crystal-lattice of ice, thus



### Strong and Weak Salts.

The number of metallic salts which are obviously "strong electrolytes" is so large that it is not always easy to realise that a salt, like an acid or base, may be a "weak electrolyte." In the following paragraphs, therefore,

<sup>8</sup> *J. Amer. Chem. Soc.*, 1920, 42, 1431; compare G. N. Lewis, *Valence*, 1923, p. 110; also Moore and Winmill, *J. Chem. Soc.*, 1912, 101, 1675.

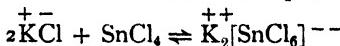
<sup>9</sup> *Phil. Mag.*, 1914 [6], 27, 757; compare Lowry, *Trans. Faraday Soc.*, 1923, 18, 285, and *Phil. Mag.*, 1923 [6], 45, 1105.

a number of examples have been brought together of salts which behave as weak electrolytes; and evidence is again cited to show that these compounds owe their peculiar inertness to the possibility of forming covalent bonds between the ions.

(a) *Stannic Chloride*.—An ionic aggregate, in which each ion is surrounded by a number of ions of opposite sign (e.g., 6 in the NaCl lattice or 8 in the CsCl lattice), provides ideal conditions for utilising the residual affinity of the ions to produce a rigid crystal structure. When therefore a substance, which has the formula of a salt, exhibits the fusibility and volatility of an organic compound, the view at once suggests itself that we are probably dealing with integral molecules, rather than with a continuous network of ions. We are therefore not surprised when stannic chloride (b.p. 114°, f.p. -33°) fails to show the electrolytic properties of a typical fused salt, since its obvious properties are those of a collection of individual molecules and not of an aggregate of ions. This general conclusion has received specific confirmation from the X-ray analysis of crystals of stannic iodide, where it has been shown that each atom of tin is surrounded tetrahedrally by four atoms of iodine, just as in the case of a covalent carbon-compound.

No data are given in the tables for the conductivity of pure stannic chloride, which appears to behave as an insulator, like pure hydrogen chloride or pure water. In aqueous solution it is hydrolysed to colloidal stannic acid  $\text{SnCl}_4 + 4\text{H}_2\text{O} \rightleftharpoons \text{Sn}(\text{OH})_4 + 4\text{HCl}$ , which appears to contribute nothing to the conductivity of the acid solution.<sup>10</sup> In liquid sulphur dioxide, however, it behaves as a weak electrolyte, giving  $\Lambda_5 = 0.008$ ,  $\Lambda_{14} = 0.04$ ,  $\Lambda_{262} = 0.262$ . Although, therefore, the metal and the halogen in stannic chloride carry complete octets of electrons, it is still possible to ionise one of the bonds; but, as the tin is then left with an outer shell of only 6 electrons, this condition is too unstable to persist except as a minor feature of the final equilibrium.

Stannic chloride can, however, be converted into a strong electrolyte by combination with potassium chloride to form potassium stannic chloride,



The crystals of this compound have been shown by X-ray analysis to be an ionic aggregate of the same type as fluorspar; but, in forming this aggregate, the tin has not been separated from the chlorine, since (if we accept Sidgwick's theory of co-ordination) it now forms part of a complex anion in which six atoms of chlorine, instead of only four, are united by real bonds to the central atom of metal. This change is obviously accompanied by conversion of a tetrahedral into an octahedral configuration. The view that an octahedral 6-co-ordination compound gives rise to a square configuration when converted into a 4-co-ordination compound, cannot therefore be maintained in this case, although it appears to have been established in the case of platinum.

(b) *Mercury Salts*.—Special interest attaches to the behaviour of the salts of mercury, since this element resembles hydrogen in the readiness with which it gives rise to "weak electrolytes," both in the molten state and in solution. This peculiar behaviour can, however, be attributed to the fact that this element, in complete defiance of the simple octet rule of the electronic theory, is equally ready to form covalent and electrovalent compounds. Evidence in support of this statement is set out in Tables I. and II. and in the paragraphs which follow.

<sup>10</sup> Foster, *Physical Rev.*, 1899, 9, 41.

TABLE I.  
SPECIFIC CONDUCTIVITY OF FUSED SALTS.

## (a) Strong Electrolytes.

$\begin{cases} \text{NaCl} \\ \text{NaBr} \\ \text{Na I} \end{cases}$	$\begin{cases} 3.34 \text{ at } 800^\circ \\ 3.06 \text{ " } \\ 2.70 \text{ " } \end{cases}$	$\begin{cases} \text{AgCl} \\ \text{AgBr} \\ \text{Ag I} \end{cases}$	$\begin{cases} 4.98 \text{ at } 800^\circ \\ 3.50 \text{ " } \\ 2.72 \text{ " } \end{cases}$	$\begin{cases} 4.48 \text{ at } 600^\circ \\ 3.18 \text{ " } \\ 2.52 \text{ " } \end{cases}$
$\begin{cases} \text{KCl} \\ \text{KBr} \\ \text{KI} \end{cases}$	$\begin{cases} 2.19 \text{ at } 800^\circ \\ 1.75 \text{ " } \\ 1.64 \text{ " } \end{cases}$	$\begin{cases} \text{Tl Cl} \\ \text{Tl Br} \\ \text{Tl I} \end{cases}$	$\begin{cases} 1.700 \text{ at } 800^\circ \\ 1.127 \text{ " } \\ 0.840 \text{ " } \end{cases}$	$\begin{cases} 1.082 \text{ at } 427^\circ \text{ (m.p.)} \\ 0.803 \text{ " } 457^\circ \\ 0.523 \text{ " } 436^\circ \end{cases}$

## (b) Weak Electrolytes.

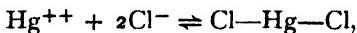
$\text{HgI}_2$	$0.0066 \text{ at } 320^\circ$	$\text{HgCl}_2$	$0.0078 \text{ at } 276^\circ \text{ (m.p.)}$
	$0.0071 \text{ " } 288^\circ$		
	$0.0085 \text{ " } 260^\circ$		
	$0.0118 \text{ " } 253^\circ \text{ (m.p.)}$		

Data for aqueous solutions of mercury-salts are as follows :—

TABLE II.  
EQUIVALENT CONDUCTIVITIES OF MERCURY SALTS.

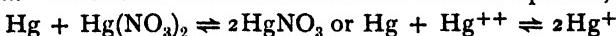
<i>Mercurous Salts.</i>		<i>Mercuric Salts.</i>	
$\text{HgClO}_4 \Lambda_{10}^{25} = 110$	$\alpha = 0.76$	$\frac{1}{2} \text{Hg(ClO}_4)_2 \Lambda_{10}^{25} = 105$	$\alpha = 0.77$
$\text{HgNO}_3 \Lambda_{32}^{18} = 59$	$\alpha = 0.56$	$\frac{1}{2} \text{Hg(NO}_3)_2 \Lambda_{32}^{25} = 6.3$	$\alpha = 0.04$
(in $N/10$ $\text{HNO}_3$ )		$\frac{1}{2} \text{HgCl}_2 \Lambda_{32}^{25} = 1.77$	$\alpha = 0.013$
		$\frac{1}{2} \text{Hg(CN)}_2 \Lambda_{10}^{25} = 0.10$	$\alpha = 0.0007$

The weak and variable electrolytic conductivities of the mercury salts are just what one might expect if the positively charged mercury ions were able to unite with the negatively-charged anions to form covalent compounds, e.g.,

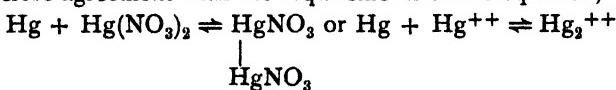


but it would be merely arguing in a circle to use these low conductivities as evidence of the formation of covalent compounds. It should be noted, however, that the conductivity of mercuric chloride is much lower than that of the nitrate, and that, whilst the coefficient of ionisation of mercuric chloride is only about 1 per cent at  $N/32$ , the two perchlorates, in which the halogen is completely enveloped by four tetrahedrally disposed atoms of oxygen, have actually passed over into the group of strong electrolytes (compare barium perchlorate) with coefficients of 76 per cent. and 77 per cent. respectively at a concentration of  $N/10$ . On the other hand, mercuric cyanide, which was described by Prussia in 1898<sup>11</sup> as a non-conductor, behaves exactly like an organic compound in which ionisation is just beginning to be possible (compare  $\text{CMe}_3\text{I}$  in liquid  $\text{SO}_2$ ).

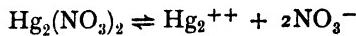
Fortunately, however, direct evidence is available to prove that mercury does actually form covalent compounds of the type that has been postulated as characteristic of "weak electrolytes." Thus, as long ago as 1898, Ogg showed<sup>12</sup> that the ratio between the two nitrates of mercury, when in equilibrium with metallic mercury and a given concentration of nitric acid, is constant. This result cannot be reconciled with the equation,



but is in close agreement with the requirements of the equation,



The mercurous ion is, therefore, not a simple charged atom  $Hg^+$  but a covalent complex  $Hg_2^{++}$ . This conclusion was confirmed by determinations of the electromotive force of concentration-cells, as well as by other methods of investigation. The later measurements by Schilow<sup>13</sup> of the transport-number and conductivity of mercurous nitrate, in aqueous solutions and in presence of dilute nitric acid, also support Ogg's conclusion that mercurous nitrate is a *ternary* electrolyte, the ionisation of which must be represented by the scheme,



and not by the simple scheme for a *binary* electrolyte,



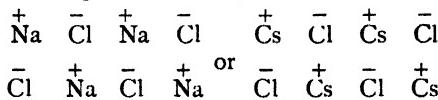
Even more conclusive are the recent observations of Havighurst<sup>14</sup> on the X-ray analysis of crystals of mercurous chloride, bromide, and iodide. Nearly all of the binary haloid salts crystallise in the cubic system, e.g.,

$NaCl$ ,  $KCl$ ,  $AgCl$ ,  $AgBr$ , on a face-centred cubic lattice,

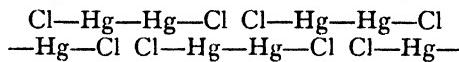
$CsCl$ ,  $CsI$ ,  $TlCl$ ,  $TlBr$ , on a body-centred cubic lattice,

$CuCl$ ,  $CuBr$ ,  $CuI$ ,  $AgI$ , on the diamond or zinc sulphide type of cubic lattice.

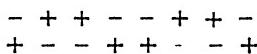
The mercurous haloids, however, all crystallise in the tetragonal system; and X-ray analysis has shown that the arrangement of the atoms of metal and halogen is not a simple alternation, as in rock salt or caesium chloride,



but an alternation of *pairs* of atoms as in the scheme,

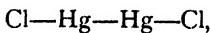


Since the scheme,

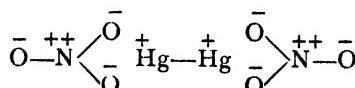


is impossible as a stable arrangement of positive and negative ions, Havighurst concludes that "The structure of these crystals indicates the existence of the chain-molecule  $Cl-Hg-Hg-Cl$ . The strong double refraction which has been observed is to be expected from a crystal having this structure."<sup>14</sup>

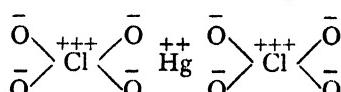
From this evidence it is clear that mercury can exhibit either a covalence of 2 as in calomel,



or a covalence of 1 and a positive electrovalence of 1 as in mercurous nitrate,



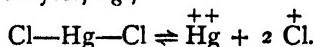
or a positive electrovalence of 2 as in mercuric perchlorate,



<sup>13</sup> Z. anorg. Chem., 1924, 133, 55.

<sup>14</sup> Am. Jour. Sci., 1925, 10, 15.

The way is therefore open for a reversible equilibrium between free ions and real molecules, of precisely the same type as has been postulated in the case of other weak electrolytes, e.g.,



(c) *Co-ordinated Salts.*—In the category of weak electrolytes we must also include a large number of co-ordination-compounds, since it is clear that, as the firmness with which a metal is co-ordinated to the negative radical is increased, its coefficient of ionisation must be diminished, or, in other words, that its efficiency as an electrolyte must decay *pari passu* with the increase of the efficiency of the co-ordination. Since, however, Sidgwick considers that the act of co-ordination consists in the formation of a bond by the transfer of an electron from one atom to another, these cases obviously fall within the limits of our specification of the principal condition for the production of weak electrolytes.

Unfortunately, data in reference to the ionisation of compounds of this type are scanty, since most of them, in losing their character as strong electrolytes, become insoluble in water, and therefore pass right over to the category of non-electrolytes, rather than of weak electrolytes. Intermediate cases, are, however, provided by the salts of organic hydroxy-acids. Thus Calame has shown by determinations of freezing-point that, whilst calcium *lactate* is ionised to the extent of 40 per cent. at a concentration of  $0.257N$ , the copper salt is ionised only to the extent of 17 per cent. at  $0.271N$ .<sup>15</sup> In the same way, Tower has reported<sup>16</sup> that, whilst the molecular conductivities of the *succinates* of Ni, Co, and Mg are very similar at all concentrations, the molecular conductivities of the *tartrate* and *malate* of cobalt and nickel are very much smaller than those either of the magnesium salts or of the corresponding succinates. Again, Calame has shown that the coefficient of ionisation of copper *malate* is only 4 per cent. in  $N/4.628$  solution, 10 per cent. in  $N/74$  solution, and 19 per cent. in  $N/592$  solution, whereas zinc *maleate* (where co-ordination is prevented by the elimination of the hydroxyl group) is dissociated to the extent of 22 per cent., 44 per cent., and 69 per cent. in solutions of similar concentrations. All these results are in accord with the view that the co-ordination of the ions of a metallic salt tends to convert it into a "weak electrolyte."

Other examples of weak electrolytes are afforded by the so-called "non-valent" co-ordination-complexes. Thus the following values are recorded for the conductivities of the ammines of platinous nitrite:<sup>17</sup>

$\text{Pt}(\text{NO}_2)_2 \cdot 4\text{NH}_3$ or $[\text{Pt} \cdot 4\text{NH}_3]^{++} (\text{NO}_2)_2^- - \Lambda_{1000}^{25} = 276.5$
$\text{Pt}(\text{NO}_2)_2 \cdot 3\text{NH}_3$ or $[\text{Pt} \cdot 3\text{NH}_3 \cdot \text{NO}_2]^{+} \text{NO}_2^- - \Lambda_{1000}^{25} = 96.5$
$\text{Pt}(\text{NO}_2)_2 \cdot 2\text{NH}_3$ or $[\text{Pt} \cdot 2\text{NH}_3 \cdot 2\text{NO}_2]^\pm - \Lambda_{1000}^{25} = 0.95$ (cis.) = 2.42 (trans.).

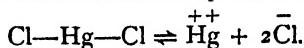
It is commonly stated that substances such as  $[\text{Pt} \cdot 2\text{NH}_3 \cdot 2\text{NO}_2]^\pm$ ,  $[\text{Pt} \cdot 2\text{NH}_3 \cdot 4\text{Cl}]^\pm$  and  $[\text{Co} \cdot 3\text{NH}_3 \cdot 3\text{NO}_2]^\pm$  are "non-electrolytes," but this statement is not in harmony with a summary of the experimental data in which it is said that "the compound is a very poor conductor of the electric current in aqueous solutions." If this description is correct, i.e., if the feeble conductivity which is observed even in freshly-prepared solutions of these compounds cannot be explained away by the hydrolysis of the complex, these "non-valent" ammines must be classed with the "weak

<sup>15</sup> *Z. physikal. Chem.*, 1898, **27**, 401.

<sup>16</sup> *J. Amer. Chem. Soc.*, 1900, **22**, 501; 1902, **24**, 1012.

<sup>17</sup> Tschugaeff and Wladimiroff, *J. Russ. ph. Ch. Ges.*, 1920, **52**, 135.

electrolytes," which exhibit a small electrolytic conductivity as a result of the reversible ionisation of a covalent complex, compare



(d) *Carbonium Salts*.—These salts are characterised by very wide range of conductivities. Thus Walden<sup>18</sup> found the following values for the equivalent conductivities of a series of halogen-salts dissolved in liquid sulphur dioxide at 0°:—

KI	$\Lambda_{96} = 59.5$	$\Lambda_{2000} = 142.3$
$(\text{C}_6\text{H}_5)_3\text{CBr}$	$\Lambda_{96} = 108.5$	$\Lambda_{2001} = 152$
$(\text{C}_6\text{H}_5)_3\text{CCl}$	$\Lambda_{105} = 15.0$	
$(\text{CH}_3)_3\text{Cl}$	$\Lambda_{17} = 0.7$	

The tertiary halides therefore cover the whole of the available range of conductivities, some of them being better conductors than a typical "strong electrolyte" like potassium iodide, whilst others have no conductivity at all. The same conclusion follows from the observations of Gomberg,<sup>19</sup> who gives the following values for the degree of dissociation of some carbonium salts at -8° and  $v = 100$ , in comparison with the value for tetramethyl-ammonium bromide,

$(\text{C}_6\text{H}_5)_3\text{CCl}$	12 per cent.	$(\text{C}_6\text{H}_5 \cdot \text{C}_6\text{H}_4)_3\text{CCl}$	45 per cent.
$(\text{C}_6\text{H}_5)_3\text{CBr}$	61 per cent.	$(\text{CH}_3)_4\text{NBr}$	56 per cent.

In all these carbonium salts the rules of valency permit the formation of a covalent bond between the carbon of the cation and the halogen of the anion, giving rise to a true molecule instead of an ionic doublet. Since the carbon-halogen bond is usually too strong to be ionised by mere dissolution

in a solvent, most of the compounds of the type  $\text{CCl} \rightarrow \text{CBr}$  or  $\text{CI} \rightarrow \text{CI}$  are non-conductors; but when the bond is weakened,<sup>20</sup> e.g., by substitution and by replacing chlorine or bromine by iodine, so that ionisation according to the scheme  $\text{CI} \rightleftharpoons \text{C}^+ + \bar{\text{I}}$  becomes possible, the compounds pass into the group of "weak electrolytes," although they do not usually exhibit this property in aqueous solutions; and, finally, when formation of a bond is rendered even more difficult<sup>20</sup> by the introduction of bulky aromatic substituents the salts are actually better conductors than many "strong electrolytes."

### Summary.

(a) Although most electrolytes are ionised completely, even in the solid state, there are many compounds in which ionisation is incomplete and reversible.

(c) Compounds of this type, in which neutralisation of the ionic charges is not prevented by the laws of valency, behave as "weak electrolytes," unless the bond between the radicals is too weak to hinder the ionisation of the molecule.

(d) "Weak electrolytes" of this class are found amongst acids and bases, pseudo-electrolytes, co-ordinated salts, and a few simple metallic salts such as mercuric chloride, where covalent molecules can be formed from the ions.

<sup>18</sup> Ber., 1902, 35, 2023.

<sup>19</sup> J. Amer. Chem. Soc., 1922, 44, 1818; 1923, 45, 206.

<sup>20</sup> Flürsheim, loc. cit., and J. Chem. Soc., 1909, 95, 718.

# THE EFFECT OF TEMPERATURE ON DIFFUSION POTENTIALS.

By E. B. R. PRIDEAUX.

(Received 29th June, 1927.)

During the course of work which has been designed to examine the relations between diffusion and membrane potentials, there has been occasion from time to time to test the variation of these with temperature over the ordinary range, in the case of alkali salts of some organic acids. No variation has been found which was above the limit of an error which was to be expected in these experiments. This constancy has some practical importance as enabling measurements to be carried out without a thermostat. A review of the ionic mobilities and transport numbers of strong electrolytes has partly confirmed the present thesis: that the temperature coefficients should be low or perhaps quite negligible over a temperature range of about  $10^{\circ}$ . Since however the existing data are insufficient, it was decided to investigate the problem in the case of a few typical electrolytes at the two standard temperatures,  $18^{\circ}$  and  $25^{\circ}$ , using the ideally sharp flowing junction, which removes the uncertainty as to whether a pure or mixed boundary is present.

## Theoretical.

In the equation— $E_d = \left( \frac{R}{nF} \right) T \times \frac{u_A - u_K}{u_A + u_K} \log \frac{a_1 c_1}{a_2 c_2}$ , the values of the

terms  $\frac{u_A - u_K}{u_A + u_K}$  at different temperature may be determined from the transport numbers or ionic mobilities, and in the first place from those at infinite dilution, if as is the case with most uni-univalent electrolytes the transport numbers do not vary within the limits of concentration taken, i.e.  $0.1 N$  and  $0.01 N$  in the present series.

Since the ionic mobilities become more nearly equal as the temperature rises,  $n_A$  or  $n_K$  decreases, and tend to compensate for the increase in the factor  $RT/nF$ . If this compensation is exact, the temperature coefficient of diffusion potentials will be zero. A few ionic mobilities at the two temperatures are taken from the list in Forster's "Elektrochemie" 1921, or (in brackets), from that in the "Smithsonian Tables."<sup>1</sup>

$t^{\circ} C.$	H <sup>+</sup> .	Na <sup>+</sup> .	K <sup>+</sup> .	Ag <sup>+</sup> .	
25	345 or 347 or 350	50.9	74.7	(63.5)	
18	313 or 314.5	43.5	64.6	54.3	
$t^{\circ} C.$	OH <sup>-</sup> .	Cl <sup>-</sup> .	NO <sub>3</sub> <sup>-</sup> .	SO <sub>4</sub> <sup>2-</sup> .	CH <sub>3</sub> COO <sup>-</sup> .
25°	192	75.5 or 75.9	(70.6)	(79)	36.2
18°	174	65.5	61.7	68	31.0

<sup>1</sup> Johnson, *J. Amer. Chem. Soc.*, 1909, 31, 1010.

## 12 EFFECT OF TEMPERATURE ON DIFFUSION POTENTIALS

The values of  $2n_A - 1$  or  $1 - 2n_A$  are given in the second and third lines respectively, and those of the ratios at the two temperatures in the third. They are to be compared with  $298/291 = 1.024$ .

$t^\circ C.$	HCl.	HNO <sub>3</sub> .	$\frac{1}{2} H_2SO_4$ .	NaOH.	KOH.
25	'644 ('641)	'655	'633 ('63)	'58	
18	'655 ('655)	'671	'644 ('640)	'595	
Ratio	1.017 (1.020)	1.025	1.016	1.025	
	NaCl.	KNO <sub>3</sub> .	AgNO <sub>3</sub> .	KOOCCH <sub>3</sub> .	HOOC . CH <sub>3</sub> .
25	'1975 or '1945	'0229	'053	'345	0.815
18	'202	'0262	'06375	'353	0.825
Ratio	1.021 or 1.040	1.14	1.20	1.021	1.010

The mean of all these ratios, 1.024, is the same as the ratio of the absolute temperatures. It seems probable that some at least of the individual variations are due to uncertainties in the values of the transport numbers; compare, for example, the alternative values for HCl and NaCl. Also, when the transport numbers are in the neighbourhood of 0.5, as in the case of KNO<sub>3</sub>, the experimental errors fall very heavily on  $2n_A - 1$ . In the case of AgNO<sub>3</sub> the ionic mobilities point to an appreciable temperature coefficient, and this will be negative, while in that of acetic acid, it will be positive.

### Experimental.

In an apparatus somewhat similar to that described by Scatchard,<sup>2</sup> a flowing junction is set up, which is supplied by two reservoirs containing the two solutions, of concentrations  $c_1$  and  $c_2$ , having equal hydrostatic pressures at the junction. A few drops of a suitable indicator may be added to  $c_1$  in order to make the boundary visible. The solutions are connected by side tubes with saturated KCl calomel electrodes. The potential differences between these, *i.e.*, the diffusion potentials were measured on a Cambridge portable potentiometer, type B, used with an external galvanometer and scale. The standard of potential was a cadmium cell, checked from time to time against an N.P.L. standard. The flowing junction and reservoirs were immersed in a small thermostat regulated by hand. The potential becomes constant at once if the junction has been properly set up, and remains so as long as the solutions are supplied. Individual readings agreed as closely as the scale permitted, *i.e.* to about 0.2 millivolt.

Solutions were made from water which had been freed from carbonic acid by a current of air free from carbon dioxide. The sodium hydroxide was freshly made from a carbonate-free stock which was kept in a silver bottle. The potassium benzoate was made from the pure acid, neutralised hot in a silica basin with standard potassium hydroxide, and finally adjusted in the presence of phenylphthalein. Potassium phenyl acetate was prepared in a similar manner. Piperidinium hydrochloride was made from a weighed quantity of the pure base, neutralised by standard acid (to methyl red), diluted to the required concentration and checked by titration with silver nitrate. The acetic acid was made from A.R. reagent, and standardised as usual.

<sup>2</sup> *J. Amer. Chem. Soc.*, 1925, 47, 698.

TABLE OF DIFFUSION POTENTIALS (IN MILLIVOLTS) WITH THEIR TEMPERATURE COEFFICIENTS.<sup>1</sup>

Electrolyte.	Experimental Diffusion Potentials.		Temperature Coefficient (Found).	Temperature Coefficient (Calculated). <sup>2</sup>	Theoretical Diffusion Potentials. <sup>3</sup>
	18°.	25°.			
HCl . . .	+ 36·9	+ 37·25	+ 0·35	+	37·8(18°)
NaOH . . .	- 35·0	- 34·6	- 0·40	0	- 34·6(18°)
NaCl . . .	- 11·75	- 11·70	- 0·05	0	- 11· (18°)
AgNO <sub>3</sub> . . .	- 3·6	- 3·4	- 0·2	-	- 3·25(18°)
C <sub>6</sub> H <sub>5</sub> N. HCl . . .	- 20·25	- 20·7	+ 0·45	?	- 20·5(25°)
KOO. C <sub>6</sub> H <sub>5</sub> . . .	+ 22·1	+ 22·15	± 0	?	+ 22·25(25°) *
KOO. CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> . . .	+ 24·0	+ 24·0	± 0	?	+ 22·25(25°) *
HOOC. CH <sub>3</sub> . . .	+ 19·5	+ 20·2	+ 0·7	+	23·75(18°) 24·1(25°)

<sup>1</sup> An increase in the numerical value is taken as positive.  
exceeds the probable error in the data.

<sup>2</sup> Where this effect  
is calculated from the ionic mobilities, etc

\* Trans. Far. Soc., 1924, 20, 37.

### Discussion of Results.

A few cases require special comment.

The diffusion potential of silver nitrate at 25° is due to Cumming.<sup>3</sup> It was measured by him at a static junction, as the difference between the potentials of two Ag, AgNO<sub>3</sub>, N/10 and N/100, concentration cells (*a*) without and (*b*) with, elimination of diffusion potential by a saturated solution of ammonium nitrate. The present value, at 18°, was also determined at a static junction, but was a direct measurement of the diffusion potential of the AgNO<sub>3</sub> concentration chain, the end electrodes being two saturated KCl calomel half-cells which were separated from the silver nitrate by saturated ammonium nitrate. Acetic acid was added as an example of a weak electrolyte, and it was of interest to ascertain whether the Planck theory applies also to this class. It is a favourable case, since the dissociation constant does not change appreciably either with the concentration, or with the temperature within the limits over which these factors were varied. The potentials were found to be as steady as usual, but do not agree as well as usual with the values deduced from the transport numbers and the ionic mobilities, the latter being calculated from the dissociation constant  $1\cdot85 \times 10^{-5}$ . Since the experimental values are lower, this may be due to a special difficulty in producing an ideally sharp junction between different concentrations of a weak electrolyte, only a small proportion of which exists as ions.

The diffusion potentials of the other electrolytes, which had been previously recorded, and obtained at static junctions are in good agreement with the present values, showing that the static junction in these cases may give a sufficiently sharp boundary. Together with the other examples, the diffusion potentials of which had not been previously determined in any manner, the Table includes all the principal types of strong electrolytes—acid, alkali, salts of strong acid and alkali, alkali and weak acid, weak base and strong acid, and a weak acid.<sup>4</sup> The diffusion potentials of all these are found to have temperature coefficients which are either zero,

<sup>3</sup> Z. Elektrochem., 1907, 13, 17.

<sup>4</sup> Electrolytes which are appreciably hydrolysed have not been investigated, these will clearly behave as mixtures of the salts with strong acids (or alkalis).

or not more than 0·5 of a millivolt (except acetic acid) for 7° within the ordinary temperature range. In the first part of this paper it has been shown that this is a consequence of the relation between temperatures and ionic mobilities.

These results may be embodied in the statement that the diffusion potentials between different concentrations of the same strong electrolytes have as a class very low temperature coefficients.

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## THE IONISATION OF POLYHYDRION ACIDS.

BY C. MORTON.

(Communicated by DR. S. SKINNER.)

(Received 1st July, 1927.) \*

The dissociation of a weak *m*-valent acid  $\text{AH}_m$  may be defined in terms of the law of mass action :—

$$K_1 = h \frac{[\text{AH}_{m-1}^-]}{[\text{AH}_m]}; K_2 = h \frac{[\text{AH}_{m-2}^-]}{[\text{AH}_{m-1}^-]}, \text{etc.} \quad . \quad . \quad . \quad (1)$$

When ionisation takes place in isolated steps, the classic dissociation constants  $K_1$ ,  $K_2$ , . . . are readily computed from the data of the neutralisation curve : for this purpose equation (1) is used in the general form

$$K = h \frac{[\text{Salt}]}{[\text{Acid}]} \quad \text{or} \quad pK = pH + \log [\text{Acid}] / [\text{Salt}] \quad . \quad . \quad . \quad (2)$$

where  $K = 10^{-pK}$  and  $h = 10^{-pH}$ .

The more difficult problem presented by tribasic acids, such as tricarballylic, camphoronic, and citric, which ionise in overlapping stages, has been examined by Enklaar<sup>1</sup> and by Auerbach and Smolczyk.<sup>2</sup> These authors determined the neutralisation curve and dissociation constants of citric acid : those of the related acids were not investigated. Enklaar computed  $K_1$  and  $K_2$  for citric acid by means of an expression identical with (2). The "constants" vary within wide limits. The computations of Auerbach and Smolczyk were based on two supposed identities :  $\gamma_2$

(a)  $h^2 = K_2 K_3$  when the acid is two-thirds neutralised ;

(b)  $h^2 = K_1 K_2 (2K_3 + h)/h$  when the acid is one-third neutralised. It may be shown that the expressions hold, not at the points on the curve corresponding to the formation of the salts  $B_2\text{HA}$  and  $\text{BH}_2\text{A}$  respectively, but at the points at which (a) the concentrations of primary and tertiary ions are equal, (b) the concentration of primary ions is maximal. The method has the further disadvantages that the calculation of  $K_1$  is based on a measurement of the hydron concentration at a single point on the neutralisation curve, and that the formula used involves the other constants.

Furthermore, the classic "dissociation constants," as ordinarily defined

<sup>1</sup> Enklaar, *Z. physikal. Chem.*, 1912, **80**, 620.

<sup>2</sup> Auerbach and Smolczyk, *ibid.*, 1924, **111**, 83.

and determined, are not true constants. Since the law of mass action, as thermodynamically conceived, relates, not to stoichiometric concentrations, but to active mass or activity, equation (1) may be restated:—

$$k_1 = a_H^{-1} \frac{[AH_m^-_1]}{\gamma_1 [AH_m]} ; k_2 = a_H^{-1} \frac{[AH_m^-_2]}{\gamma_2 [AH_m^-_1]}, \text{etc. . . .} \quad (3)$$

$\gamma_1, \gamma_2, \gamma_3, \dots$  are the activity coefficients of the species  $AH_m$ ,  $AH_m^-_1$ ,  $AH_m^-_2, \dots$ . Hence the relationship between the true dissociation constant  $k_x$  and the classic constant  $K_x$  for the  $x$ th stage in the dissociation of the acid is given by

$$\rho k_x = \rho K_x + \log (\gamma_{x-1}/\gamma_x) . . . . . \quad (4)$$

For temperature not far removed from normal, the Debye-Hückel<sup>3</sup> equation for the activity coefficient  $\gamma$  of an ion of valency  $v$  may be put in the form,

$$-\log \gamma = .5v^2 \sqrt{\mu} / (1 + \beta \sqrt{\mu}) . . . . . \quad (5)$$

where  $\mu$  is the ionic strength as defined by Lewis and Randall.<sup>4</sup>  $\beta$  is the proportionality constant of a correction term expressing the effective thickness of the ionic atmosphere and the mean effective diameter of the ions. Equation (4) may now be written,

$$\rho k_x = \rho K_x + (x - .5) \sqrt{\mu} / (1 + \beta \sqrt{\mu}) . . . . . \quad (6)$$

From the data of the neutralisation curve,  $\rho K_x$  may be computed by means of equation (2).  $\beta$  is obtained by plotting  $\rho K_x$  against  $\sqrt{\mu}$  and extrapolating to infinite dilution; equation (6) then gives  $k_x$ , the true dissociation constant.

The classic measurements of Walpole,<sup>5</sup> Sörensen, and Clark and Lubs<sup>6</sup> provide excellent material for testing the reliability of the theory.

TABLE I.—WALPOLE'S STANDARD ACETATE MIXTURES.

$\rho_H$	2.696	2.804	2.912	2.994	3.081	3.147	3.202	3.315	3.416	3.592	3.723	4.047	4.270
$K \times 10^5$	2.04	2.07	2.02	2.06	2.06	2.10	2.14	2.16	2.08	2.13	2.12	2.25	1.31
$k \times 10^5$	1.95	1.96	1.91	1.94	1.92	1.95	1.95	1.99	1.90	1.92	1.89	1.95	.96
	2.37												
$\rho_H$	4.626	4.802	4.990	5.093	5.227	5.374	5.574	5.894	6.024	6.211	6.518	7.200	
$K \times 10^5$	2.37	2.39	2.42	2.37	2.39	2.40	2.43	2.43	2.45	2.45	2.40	2.52	
$k \times 10^5$	1.96	1.94	1.95	1.97	1.92	1.93	1.93	1.93	1.95	1.96	1.92	2.01	

Mean value of  $k \times 10^5 = 1.94$ .

In Table I. the  $K$  and  $k$  values of acetic acid, computed from Walpole's neutralisation measurements in  $0.2 M$  solution, are given. The  $K \times 10^5$  values rise from 2.02 to 2.52 as the ionic strength increases: for the sodium acetate-HCl mixtures the values are higher (2.40–2.86).

TABLE II.—WALPOLE'S ACETATE—HCl MIXTURES.

$\rho_H$	6.31	5.87	5.20	4.95	4.76	4.58	4.39	4.19	3.95	3.79	3.61	3.49	3.33	3.09	3.04
$K \times 10^5$	2.40	2.44	2.53	2.61	2.61	2.63	2.71	2.77	2.80	2.86	2.74	2.07	2.73	2.55	2.82
$k \times 10^5$	1.80	1.83	1.88	1.93	1.92	1.92	1.97	2.00	2.01	2.01	1.97	1.96	1.86	1.80	2.01

Mean value of  $k \times 10^5 = 1.93$ .

<sup>3</sup> Debye and Hückel, *Physikal. Z.*, 1923, 24, 185; Hückel, *ibid.*, 1925, 26, 93; Brönsted and La Mer, *J. Amer. Chem. Soc.*, 1924, 46, 555.

<sup>4</sup> Lewis and Randall, *ibid.*, 1921, 43, 1112.

<sup>5</sup> Walpole, *J.C.S.*, 1914, 105, 2501, 2521.

<sup>6</sup> Clark and Lubs, *J. Biol. Chem.*, 1916, 25, 479.

The corresponding  $k \times 10^5$  values are nearly constant and equal in the two series, the mean values being 1.94 and 1.93 respectively. The measurements of Kendall,<sup>7</sup> recently recalculated by MacInnes<sup>8</sup> point to a somewhat lower value, with which the results of the author's electrometric titration in '01M solution agree (Table III.).

TABLE III.

## POTENTIOMETRIC TITRATION OF 10 C.C. OF '01 M ACETIC ACID WITH '01 N NaOH

C.c. of NaOH .	'27	'67	1.24	2.92	3.78	5.22	6.11	7.04
E.M.F. in volts	'4554	'4670	'4806	'5055	'5153	'5306	'5400	'5505
$\rho_H$ . . .	3.522	3.715	3.941	4.354	4.517	4.773	4.928	5.102
$K \times 10^5$ . .	1.85	1.85	1.82	1.88	1.88	1.91	1.87	1.89
$k \times 10^5$ . .	1.80	1.79	1.75	1.78	1.77	1.78	1.74	1.66
C.c. of NaOH .	7.97	8.59	9.10	9.40	9.61	9.74	9.85	9.91
E.M.F. in volts	'5637	'5752	'5886	'5995	'6110	'6225	'6368	'6486
$\rho_H$ . . .	5.322	5.513	5.737	5.919	6.110	6.301	6.539	6.738
$K \times 10^5$ . .	1.88	1.86	1.86	1.89	1.93	1.94	1.89	2.07
$k \times 10^5$ . .	1.74	1.72	1.72	1.75	1.78	1.79	1.75	1.91
C.c. of NaOH .	9.94	9.97	9.990	10.04	10.2	10.49	11.5	
E.M.F. in volts	'6616	'6833	'7060	'7855	'8230	'8461	'8785	
$\rho_H$ . . .	6.950	7.313	7.690	9.012	9.636	10.02	10.56	
$K \times 10^5$ . .	2.00	—	—	—	—	—	—	
$k \times 10^5$ . .	1.84	—	—	—	—	—	—	

$$\text{Mean values: } K \times 10^5 = 1.90 \quad k \times 10^5 = 1.77.$$

With a view to testing the applicability of equation (6) to polyhydrion acids, the  $K_2$  and  $k_2$  values of phthalic and phosphoric acids have been computed from data provided by the Clark and Lubs' phthalate and  $\text{KH}_2\text{PO}_4$  - NaOH mixtures (Tables IV.-V.).

TABLE IV.—CLARK &amp; LUBS' PHTHALATE—NaOH MIXTURES.

$\rho_H$ .	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0
$K_2 \times 10^6$	7.03	8.07	8.69	9.14	9.42	9.71	9.86	9.75	10.00
$k_2 \times 10^6$	3.14	3.44	3.50	3.47	3.39	3.34	3.28	3.18	3.20

TABLE V.—CLARK & LUBS'  $\text{KH}_2\text{PO}_4$  - NaOH MIXTURES.

$\rho_H$ .	5.8	6.0	6.2	6.4	6.6	6.8	7.0	7.2	7.4	7.6
$K_2 \times 10^7$	1.27	1.29	1.31	1.34	1.38	1.42	1.46	1.47	1.50	1.49
$k_2 \times 10^7$	7.23	7.19	7.21	7.21	7.26	7.24	7.24	7.19	7.19	7.10

In solutions of lower acidity than that denoted by  $\rho_H = 4$ , the ionic equilibria in these and in Walpole's buffer mixtures are described, in general with an accuracy of  $\pm 0.01 \rho_H$ , by the expression,

$$\rho_H = \rho k_x - \log \frac{[\text{Acid}]}{[\text{Salt}]} - \frac{(x - 0.5)\sqrt{\mu}}{1 + \beta\sqrt{\mu}} \quad . . . \quad (7)$$

where  $\rho k_x = 4.71$ ,  $\beta = 2.94$  for the acetate-acetic acid mixtures

" " 4.71, " 1.84 " acetate - HCl mixtures

" " 7.14, " 1.93 "  $\text{KH}_2\text{PO}_4$  - NaOH mixtures

" " 5.48, " 0.37 " phthalate - NaOH "

<sup>7</sup> Kendall, *J.C.S.*, 1912, 101, 1275.

<sup>8</sup> MacInnes, *J. Amer. Chem. Soc.*, 1926, 48, 2068.

Equation (7) fails, however, to represent adequately the course of ionisation of polyhydron acids for which  $K_{a-1}/K_a < 10^8$ : a method of computation which yields satisfactory results in such cases is outlined in the concluding section.

The dissociation constants of the related acids, tricarballylic, camphoronic, and citric, have been computed from data obtained by potentiometric titration of approximately  $0.1M$  solutions of the acids with NaOH of the same normality. The salt concentration at the inflexion point, where the ionic strength is greatest, was thus only  $0.025M$ , and the activity correction becomes of small significance. The values of the constants which satisfied the titration data were found to be (see following table).

These results are in general agreement with the known effects of substitution on the strength of acids. Displacement of hydrogen in tricarballylic acid by the hydroxyl group increases the activity of the first or most active dissociation: the entry of the methyl group, on the other hand, diminishes the ionising power in each stage, most markedly in the case of the third or weakest dissociation.

### Experimental.

The titrations were carried out at  $30^\circ C$ . The hydrogen electrode was used, with a saturated calomel half-cell as the reference electrode, and

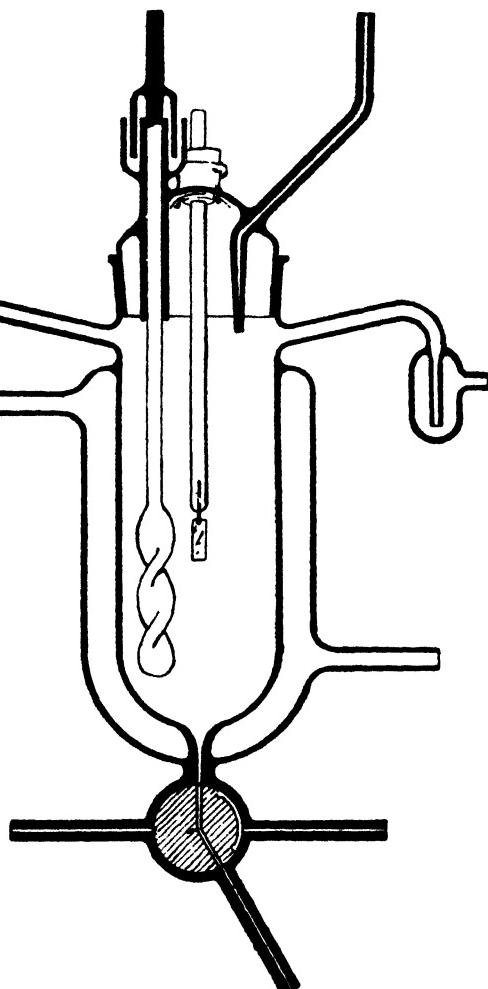
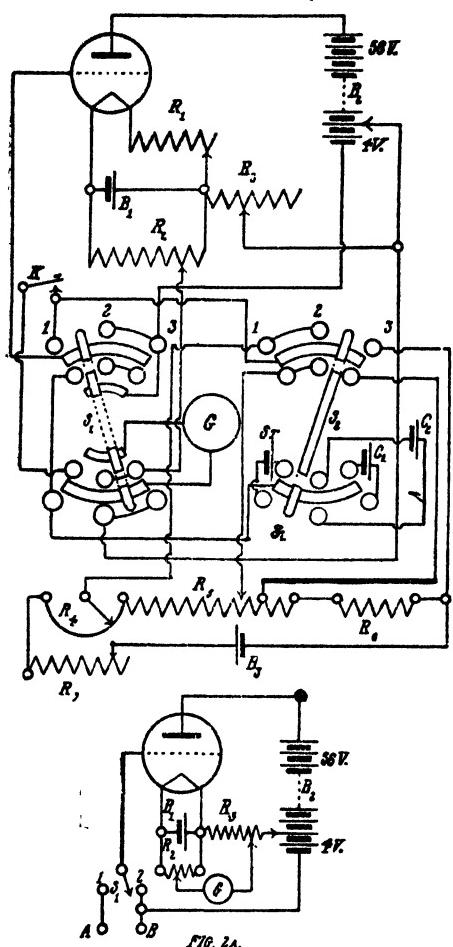


FIG. 1.—Hydrogen Electrode Titration Vessel.

	$k_1 \times 10^4$ .	$k_2 \times 10^5$ .	$k_3 \times 10^6$ .
Tricarballylic acid . . . .	3.25	2.65	1.48
Camphoronic acid . . . .	2.95	1.05	0.37
Citric acid . . . . .	9.21	2.59	1.35

saturated KCl solution forming the salt bridge. Hydrogen was obtained by electrolysis of 15 per cent. NaOH, using electrodes of pure nickel.

FIG. 2.



$B_1, B_3$  2-volt Accumulators.

$B_2$  60-volt Dry Battery.

$C_1, C_2$  Cells whose E.M.F.'s are to be determined.

St. Standard Weston Cell.

$R_1$  30  $\Omega$  Variable Resistance.

$R_2, R_3$  300  $\Omega$  Potential Dividers.

$R_4$  Potentiometer Slide Wire.

$R_5$  " Main Resistance.

$R_6$  " Standard Cell Compensating Resistance.

$R_7$  " Rheostat.

G Galvanometer.

K Tapping Key.

$S_1, S_2$  Three-position switches.

### The Hydrogen Electrode Vessel.

A water-jacketed titration vessel was used (Fig. 1). The four-position stopcock has a single bore and a groove cut in the circumference, by means of which any one of the following connections may be made: (1) Vessel to drain; (2) Hydrogen to vessel; (3) Salt bridge to drain; (4) Salt bridge to vessel. Temperature and electrical equilibrium are attained in about three minutes when the reactant is added in small increments. Water from an electrically-controlled thermostat is circulated by means of an "Albany" gear pump through jackets surrounding both hydrogen and calomel electrodes.

### The Potentiometric System.

In a lengthy titration it is necessary to interpose several closed stopcocks between the hydrogen and calomel electrodes, and the resistance of the cell is high, especially over the important range  $p_H$  6-8 of the neutralisation. To facilitate the process of balancing, a thermionic valve amplifier was used: the circuit is represented in Fig. 2, and in a simplified form in Fig. 2a. The arrangement differs fundamentally from that of Goode in that the E.M.F. readings are given, not by a roughly calibrated galvanometer in the anode circuit, but by a standard potentiometer in the grid circuit: the results cannot be vitiated by variations in battery voltages.

The mode of operation is as follows: With the switch  $S_1$  set to Position 2, the grid of the valve is connected, through

a four-volt tapping on the 60 volt dry battery  $B_2$ , with the positive terminal of the filament accumulator  $B_1$ : the normal grid potential is thus about - 2 volts with respect to the negative end of the filament. The component of

the normal anode current flowing through the galvanometer is balanced out by adjustment of  $R_4$ . The leads A and B (Fig. 2a) of the amplifier unit are connected to the "galvanometer" terminals of a standard potentiometer, to which the standard cell, the cells under examination, and a two-volt accumulator are joined in the usual manner: these connections are shown in detail in Fig. 2 below and to the right of  $S_1$ . The switch  $S_1$  is thrown over to Position 1. The remaining operations follow the normal course of potentiometric technique, the system being balanced (1) by adjustment of  $R_7$  with the standard cell in circuit, (2) by adjustment of  $R_4$  and  $R_6$  with the cells under investigation in circuit. Since on the completion of each adjustment the galvanometer is undeflected, it follows that the anode current and grid voltage are maintained constant. The potential difference between the points A and B is therefore zero, which is the condition of balance in any potentiometric system. The readings can be checked at any stage by throwing  $S_1$  over to Position 3, and measuring the *E.M.F.* by the normal direct method. Using a Marconi DE 6 valve, with a normal grid potential of -2 volts with respect to the negative end of the filament, the grid current is of the order of  $10^{-8}$  amperes, and risk of polarisation of the standard cell or of the cell under examination is eliminated. The sharpness of balance is independent of the resistance of the cell. If necessary, a correction can be applied for the slight potential drop due to the minute grid current and the resistance of the grid circuit: in general the correction is of the order of  $10^{-5}$  volts per 1000 ohms.

*Method of Standardisation.*—It is well known that the end-point of a titration is most readily determined by plotting  $\Delta E/\Delta V$ , the tangent to the neutralisation curve, against  $V$ , the volume of reactant added. By a simple modification of the above procedure it was found possible to obtain by direct experiment the values required for constructing the differential curve of Hotstetter and Roberts,<sup>9</sup> and thus to standardise the solutions simultaneously with the determination of the neutralisation curve. The method is illustrated in the case of tricarballylic acid (Fig. 3). The alkali was added in increments of 0.5 c.c., and the system balanced at each stage as described in connection with Fig. 2, thus yielding data for constructing the neutralisation curve. At each stage, after balancing, a small increment of 0.05 c.c. was added, and the resulting deflection D of the galvanometer noted before the addition of the next larger increment. The deflection D being proportional to  $\Delta E/\Delta V$ , from the curve obtained by plotting values of D against the corresponding total volume  $V$  of reagent added, the equivalence point may be located with an error of  $\pm 1/40$  c.c. This does not represent the limit of accuracy obtainable: owing to the amplifying properties of the valve, measurable deflections of a sensitive galvanometer are produced by increments of 1/100 c.c. or less of strong base. By adjusting the galvanometer shunt so that a variation of 0.00019837 T volts in grid potential (corresponding to unit  $p_H$  change) results in a deflection of 10 large divisions of the scale, the galvanometer may be made to give directly the  $p_H$  change produced by each increment of reactant: the calibration is independent of the nature of the reference electrode. The method of standardisation is, of course, applicable to all reactions which can be followed electrometrically.

The standard alkali was obtained by the action of  $CO_2$ -free water on sodium amalgam, prepared by electrolysis of pure sodium chloride with pure

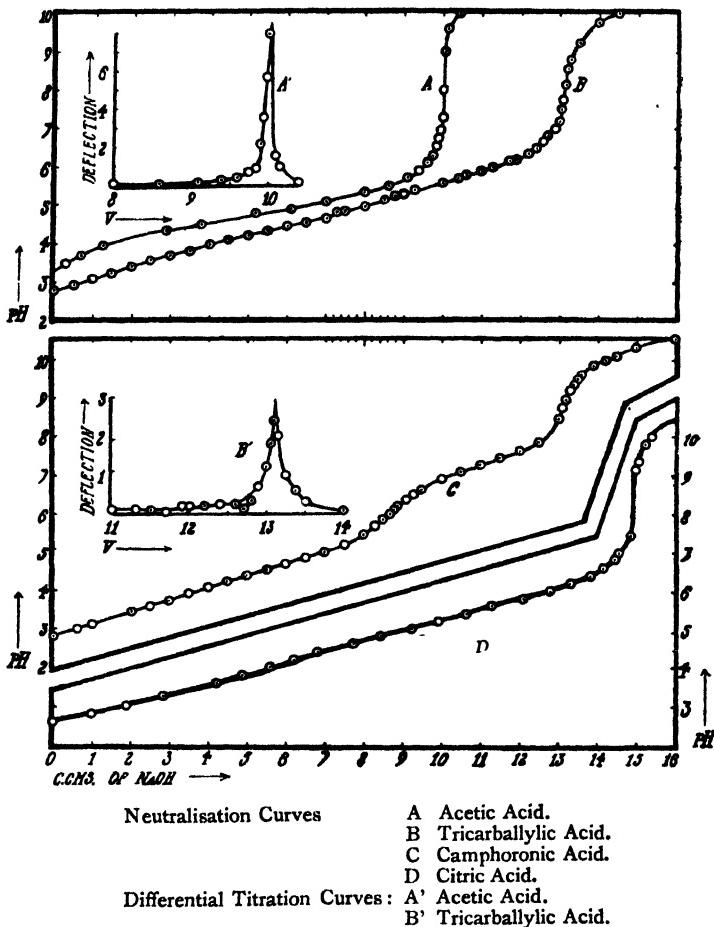
<sup>9</sup> Hotstetter & Roberts, *J. Amer. Chem. Soc.*, 1919, 41, 1341; Cox, *ibid.*, 1925, 47, 2138; MacInnes & Jones, *ibid.*, 1926, 48, 2831.

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mercury as kathode. The alkali was standardised, using the differential method described above, by titration with 0.01 N HCl prepared from constant boiling acid.

*The Method of Computation.*—In deriving the fundamental equation (15), only one assumption has been made, *viz.*, that the equilibria in solutions of weak acids and of their salts may be described in terms of the

FIG. 3



law of mass action. In a solution of the  $m$ -valent acid  $\text{AH}_m$  of molar concentration  $C_a$  we have,

$$[\text{AH}_m] + [\text{AH}_{m-1}^-] + [\text{AH}_{m-2}^{--}] + \dots = C_a \quad \dots \quad (8)$$

Let  $[\text{AH}_m] = \rho C_a$ ,  $[\text{AH}_{m-1}^-] = a_1 C_a$ ,  $[\text{AH}_{m-2}^{--}] = a_2 C_a$  and so on.

Then  $\Sigma_m a = 1 - \rho \quad \dots \quad \dots \quad \dots \quad (9)$

By equation (3),

$$k_1 = a_{\text{H}}^m \cdot \frac{\gamma_1}{\gamma} \frac{a_1}{\rho}; \quad k_2 = a_{\text{H}} \cdot \frac{\gamma_2}{\gamma_1} \frac{a_2}{a_1}; \quad \dots \quad k_m = a_{\text{H}} \cdot \frac{a_m}{a_{m-1}} \cdot \frac{\gamma_m}{\gamma_{m-1}}. \quad (10)$$

Since the undissociated molecules  $AH_m$  have no electric charge the activity coefficient  $\gamma = 1$ . Equation (8) may now be rewritten —

$$\rho = \frac{1}{1 + \frac{k_1}{a_H \gamma_1} + \frac{k_1 k_2}{a_H^2 \gamma_2} + \frac{k_1 k_2 k_3}{a_H^3 \gamma_3} + \dots + \frac{k_1 k_2 \dots k_m}{a_H^m \gamma_m}}. \quad (11)$$

Let any given amount of a strong monacid base  $BOH$  be added. The relationships developed above hold good, provided  $C_a$  be taken to mean the total acid, free and combined. Let the molar concentration of total base be  $C_b$ . By the electro-neutrality principle,

$$C_a(a_1 + 2a_2 + 3a_3 + \dots + ma_m) = C_b + h - K_w/h = \omega(\text{say})$$

Hence

$$\frac{k_1}{a_H \gamma_1} \rho + 2 \frac{k_1 k_2}{a_H^2 \gamma_2} \rho + 3 \cdot \frac{k_1 k_2 k_3}{a_H^3 \gamma_3} \rho + \dots + \frac{m k_1 k_2 \dots k_m}{a_H^m \gamma_m} \rho = \frac{\omega}{C_a}. \quad (12)$$

Thus for a tribasic acid,

$$\frac{k_1 a^2 H / \gamma_1 + 2k_1 k_2 a_H / \gamma_2 + 3k_1 k_2 k_3 / \gamma_3}{a^3 H + k_1 a^2 H / \gamma_1 + k_1 k_2 a_H / \gamma_2 + k_1 k_2 k_3 / \gamma_3} = \frac{\omega}{C_a}. \quad (13)$$

$$\begin{aligned} \text{Let } \Delta &= a^2 H (\omega - C_a) / \gamma_1, \quad \theta = a_H (\omega - 2C_a) / \gamma_2, \\ \psi &= (3C_a - \omega) / \gamma_3, \quad \phi = a^3 H \omega. \end{aligned}$$

Then

$$k_1 = \frac{\phi}{k_2 k_3 \psi - k_2 \theta - \Delta}; \quad k_2 = \frac{k_1 \Delta + \phi}{k_1 k_3 \psi - k_1 \theta}; \quad k_3 = \frac{k_1 k_2 \theta + k_1 \Delta + \phi}{k_1 k_2 \psi}. \quad (14)$$

If now three points on the titration curve be selected, the parameters of these points being

(a)  $\phi_1, \psi_1, \theta_1, \Delta_1$ ; (b)  $\phi_2, \psi_2, \theta_2, \Delta_2$ ; (c)  $\phi_3, \psi_3, \theta_3, \Delta_3$ , we obtain finally

$$\left. \begin{aligned} k_1 &= \frac{(\phi_1 \psi_3 - \psi_1 \phi_3)(\theta_1 \psi_3 - \psi_1 \theta_3) - (\theta_1 \psi_2 - \psi_1 \theta_2)(\phi_1 \psi_3 - \psi_1 \phi_3)}{(\psi_1 \Delta_2 - \Delta_1 \psi_2)(\theta_1 \psi_3 - \psi_1 \theta_3) - (\theta_1 \psi_2 - \psi_1 \theta_2)(\psi_1 \Delta_3 - \Delta_1 \psi_3)} \\ k_2 &= \frac{(\Delta_1 \psi_3 - \Delta_2 \psi_1)(\psi_1 \phi_3 - \psi_3 \phi_1) - (\Delta_1 \psi_3 - \Delta_3 \psi_1)(\psi_1 \phi_2 - \psi_2 \phi_1)}{(\theta_1 \psi_3 - \theta_3 \psi_1)(\psi_1 \phi_2 - \psi_2 \phi_1) - (\theta_1 \psi_2 - \theta_2 \psi_1)(\psi_1 \phi_3 - \psi_3 \phi_1)} \\ k_3 &= \frac{(\theta_3 \phi_1 - \theta_1 \phi_3)(\Delta_2 \phi_1 - \Delta_1 \phi_2) - (\theta_2 \phi_1 - \theta_1 \phi_2)(\Delta_3 \phi_1 - \Delta_1 \phi_3)}{(\phi_1 \psi_3 - \psi_1 \phi_3)(\Delta_2 \phi_1 - \Delta_1 \phi_2) - (\phi_1 \psi_2 - \psi_1 \phi_2)(\Delta_3 \phi_1 - \Delta_1 \phi_3)} \end{aligned} \right\} \quad (15)$$

$C_a$  and  $C_b$ , the concentrations of total acid and base respectively, are known from the amounts of acid and base, or of salts, used in the preparation of the solutions. The *E.M.F.* measurements give  $a_H$ , the hydrogen ion activity. The activity coefficients  $\gamma_1, \gamma_2$  and  $\gamma_3$  may be computed by means of the Debye-Hückel equation. In order to evaluate the remaining term,  $\omega = C_b + h - K_w/h$ , we must know  $h$ , the true hydrogen ion concentration. This is connected with the observed hydrogen ion activity  $a_H$  by means of the relationship  $a_H = \gamma_H h$ . The activity coefficient of the hydrogen ion, *viz.*,  $\gamma_H$ , may be calculated by means of the Debye-Hückel equation:  $h$  and therefore  $k_1, k_2$ , and  $k_3$  may then be obtained.

Equation (15) was used in computing the dissociation constants of citric and tricarboxylic acids. In the case of camphoronic acid, the ratio  $k_2/k_3$  is greater, and the hydronium activity at a given point on the curve is determined

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TABLE VI.—POTENTIOMETRIC TITRATION OF 5 C.C. OF 0.009906 M TRICARBALLYLIC ACID WITH 0.0113 N NaOH.

Approximate Constants Computed from Equation (19).

C.c. of NaOH .	0·0	·53	1·0	1·5	2·0	2·5	3·0	3·5	4·0	4·5
E.M.F. in volts	·4130	·4214	·4307	·4400	·4492	·4585	·4666	·4735	·4824	·4899
$\dot{\rho}_H$ . . .	2·82	2·96	3·11	3·265	3·42	3·575	3·71	3·82	3·97	4·10
$k_1 \times 10^4$ . .	2·72	3·53	3·57	3·90	3·72	4·22	4·94	6·97	14·5	—
$k_2 \times 10^6$ . .	—	—	—	—	—	—	—	—	—	·35
C.c. of NaOH .	5·0	5·5	6·0	6·5	7·0	7·3	7·5	7·6	8·0	8·2
E.M.F. in volts	·4978	·5040	·5120	·5178	·5270	·5325	·5359	·5378	·5145	·5484
$\dot{\rho}_H$ . . .	4·23	4·33	4·46	4·56	4·71	4·81	4·86	4·89	5·00	5·07
$k_1 \times 10^6$ . .	1·07	1·09	2·04	2·40	3·21	3·14	3·38	2·85	4·75	5·81
C.c. of NaOH .	8·5	8·6	8·8	9·0	9·3	9·5	10·0	10·2	10·4	10·6
E.M.F. in volts	·5531	·5550	·5580	·5610	·5666	·5697	·5789	·5829	·5859	·5919
$\dot{\rho}_H$ . . .	5·15	5·18	5·23	5·28	5·37	5·42	5·58	5·64	5·69	5·79
$k_1 \times 10^6$ . .	11·7	19·4	—	—	—	—	—	—	—	—
$k_2 \times 10^6$ . .	—	—	·07	·50	·57	·76	·105	·22	·21	·16
C.c. of NaOH .	10·8	11·0	11·3	11·5	11·7	11·9	12·0	12·2	12·4	12·6
E.M.F. in volts	·5940	·5977	·6033	·6085	·6122	·6154	·6197	·6263	·6337	·6443
$\dot{\rho}_H$ . . .	5·83	5·89	5·98	6·07	6·13	6·18	6·26	6·365	6·49	6·67
$k_1 \times 10^6$ . .	1·31	1·36	1·43	1·44	1·47	1·63	1·51	1·57	1·60	1·53
C.c. of NaOH .	12·65	12·7	12·75	12·8	12·85	12·9	12·95	13·0	13·05	13·1
E.M.F. in volts	·6470	·6519	·6534	·6585	·6619	·6653	·6723	·6770	·6935	·7098
$\dot{\rho}_H$ . . .	6·71	6·79	6·81	6·90	6·96	7·01	7·13	7·21	7·48	7·75
$k_1 \times 10^6$ . .	1·53	1·44	1·57	1·46	1·63	1·73	1·63	2·08	1·75	1·57
C.c. of NaOH .	13·15	13·2	13·25	13·3	13·35	13·5	14·0	14·5	—	—
E.M.F. in volts	·7337	·7566	·7615	·7718	·7815	·7981	·8308	·8476	—	—
$\dot{\rho}_H$ . . .	8·15	8·53	8·62	8·79	8·95	9·22	9·77	10·05	—	—

TABLE VIa.—THE DISSOCIATION CONSTANTS OF TRICARBALLYLIC ACID.

C.c. of NaOH	{	5·0 0·53 10·0	5·5 1·0 10·2	6·0 1·5 10·6	6·5 2·0 10·8	7·0 2·5 11·0	7·5 3·0 11·3	8·0 3·5 11·5
$k_1 \times 10^4$ . .		3·72	3·25	3·46	3·05	3·27	3·12	2·90
$k_2 \times 10^6$ . .		2·39	2·98	2·52	2·67	2·79	2·47	2·74
$k_3 \times 10^6$ . .		1·58	1·63	1·40	1·53	1·52	1·39	1·33

Mean values:  $k_1 \times 10^4 = 3·25$ ;  $k_2 \times 10^6 = 2·65$ ;  $k_3 \times 10^6 = 1·48$ .

by two dissociations only. For the first half of the neutralisation curve then, we may write

$$k_1 = \phi / (- k_2 \theta - \Delta); \quad k_2 = (k_1 \Delta + \phi) / (- k_1 \theta). \quad . \quad . \quad (16)$$

and by selecting two points from this portion of the curve,  $k_1$  and  $k_2$  may be obtained.

$$k_1 = \frac{\theta_1 \phi_2 - \theta_2 \phi_1}{\Delta_1 \theta_2 - \Delta_2 \theta_1}; \quad k_2 = \frac{\phi_1 \Delta_2 - \phi_2 \Delta_1}{\theta_1 \phi_2 - \theta_2 \phi_1} \quad . \quad . \quad (17)^{10}$$

<sup>10</sup> For a dibasic acid equation (17) is exact. If the activity correction be disregarded and  $K_w/h$  assumed to be negligibly small, equation (17) becomes identical with that used by Britton, *J.C.S.*, 1925, 127, 1896. For a monobasic acid,  $k = - \phi/\Delta$ .

TABLE VII.—POTENTIOMETRIC TITRATION OF 5 C.C. OF 0.0104 M CAMPHORONIC ACID WITH 0.013 N NaOH.

Approximate constants computed by equation (19).

C.c. of NaOH .	0·0	0·6	1·0	2·0	2·5	3·0	3·5	4·0	4·5
E.M.F. in volts	'4112	'4248	'4325	'4520	'4605	'4700	'4800	'4904	'5000
$\dot{\rho}_H$ . . .	2·787	3·01	3·141	3·465	3·607	3·765	3·931	4·104	4·264
$k_1 \times 10^4$ . .	3·04	2·98	3·10	3·17	3·43	3·63	4·21	4·68	5·05
C.c. of NaOH .	5·0	5·5	6·0	6·5	7·0	7·5	8·0	8·3	8·4
E.M.F. in volts	'5086	'5176	'5270	'5371	'5464	'5579	'5729	'5860	'5895
$\dot{\rho}_H$ . . .	4·407	4·557	4·728	4·881	5·036	5·227	5·476	5·695	5·753
$k_2 \times 10^5$ . .	'41	'71	'83	'94	1·01	1·00	'96	'84	1·07
C.c. of NaOH .	8·5	8·6	8·7	8·8	8·9	9·0	9·1	9·2	9·3
E.M.F. in volts	'5955	'5988	'6051	'6095	'6155	'6197	'6256	'6290	'6335
$\dot{\rho}_H$ . . .	5·853	5·924	6·012	6·086	6·185	6·255	6·353	6·410	6·485
$k_3 \times 10^8$ . .	'79	'80	'78	'86	—	—	—	—	—
C.c. of NaOH .	9·4	9·5	10·0	10·5	11·0	11·5	12·0	12·5	13·0
E.M.F. in volts	'6372	'6415	'6570	'6679	'6789	'6899	'7020	'7166	'7534
$\dot{\rho}_H$ . . .	6·55	6·62	6·88	7·06	7·24	7·42	7·63	7·87	8·48
$k_3 \times 10^8$ . .	—	—	2·76	3·48	3·64	3·74	3·74	3·36	1·58
C.c. of NaOH .	13·1	13·2	13·3	13·4	13·5	13·6	13·7	13·8	13·9
E.M.F. in volts	'7700	'7815	'7950	'8043	'8129	'8202	'8260	'8298	'8348
$\dot{\rho}_H$ . . .	8·76	8·95	9·17	9·33	9·47	9·59	9·69	9·75	9·84
C.c. of NaOH .	14·0	14·2	14·5	15·0	16·0	16·7	17·4	18·1	18·8
E.M.F. in volts	'8390	'8471	'8556	'8646	'8773	19·54	20·24	20·94	21·64
$\dot{\rho}_H$ . . .	9·90	10·04	10·10	10·33	10·54	—	—	—	—

TABLE VIIa.—THE DISSOCIATION CONSTANTS OF CAMPHORONIC ACID.

V <sub>B</sub> .	$k_1 \times 10^4$ .	$k_2 \times 10^5$ .	V <sub>B</sub> .	$k_2 \times 10^5$ .	$k_3 \times 10^8$ .
0·0}	3·00	1·02	7·0}	1·00	3·65
5·0}			10·5}		
0·6}	2·91	1·11	7·5}	1·00	3·72
5·5}			11·5}		
1·0}	3·00	1·05	12·5}	1·00	3·38
6·0}			7·0}		
2·0}	2·91	1·08	12·0}	1·05	3·76
6·5}			7·5}		
2·5}	2·98	1·11	11·0}	1·00	3·72
7·0}			7·0}		
3·0}	2·90	1·08	8·4}	(7·38)	3·77
7·5}			12·0}		

Mean values :  $k_1 \times 10^4 = 2·95$ ;  $k_2 \times 10^5 = 1·05$ ;  $k_3 \times 10^8 = 3·7$ .

$\theta_1$ ,  $\phi_1$ ,  $\Delta_1$  and  $\theta_2$ ,  $\phi_2$ ,  $\Delta_2$  are the parameters of the two points in question. A similar method was used in determining  $k_2$  and  $k_3$  from the remaining portion of the curve :—

$$k_2 = \frac{\Delta_1 \psi_2 - \Delta_2 \psi_1}{\psi_1 \theta_2 - \psi_2 \theta_1}; \quad k_3 = \frac{\Delta_1 \theta_2 - \Delta_2 \theta_1}{\Delta_1 \psi_2 - \Delta_2 \psi_1} \quad . \quad . \quad . \quad (18)$$

The approximate values given in Tables VI., VII., and VIII. were calculated by assuming that

$$k_1 = -\phi/\Delta; \quad k_2 = -\Delta/\theta; \quad k_3 = \theta/\psi \quad . \quad . \quad . \quad (19)$$

## THE IONISATION OF POLYHYDRION ACIDS

TABLE VIII.—POTENTIOMETRIC TITRATION OF 10 C.C. OF '01 M CITRIC ACID WITH '01 M NaOH.

Approximate Constants Computed from Equation (19).

C.c. of NaOH . . .	0·0	1·95	3·81	5·66	6·90	8·43	9·74	11·14	12·39	
E.M.F. in volts . . .	'3991	'4124	'4253	'4386	'4480	'4608	'4726	'4854	'4966	
$\bar{h}_H$ . . .	2·585	2·807	3·021	3·242	3·399	3·612	3·808	4·021	4·207	
$k_1 \times 10^4$ . . .	9·14	9·62	10·0	10·9	12·5	19·4	—	—	—	
$k_2 \times 10^6$ . . .	—	—	—	—	—	—	'08	1·48	2·10	
C.c. of NaOH . . .	13·70	15·48	16·90	18·51	19·85	21·25	22·64	24·16	25·53	
E.M.F. in volts . . .	'5076	'5216	'5327	'5455	'5566	'5682	'5796	'5924	'6045	
$\bar{h}_H$ . . .	4·390	4·623	4·808	5·021	5·205	5·398	5·588	5·801	6·002	
$k_1 \times 10^4$ . . .	2·50	2·96	3·54	5·55	46·9	—	—	—	—	
$k_2 \times 10^6$ . . .	—	—	—	—	—	'58	'94	1·13	1·23	
C.c. of NaOH . . .	26·70	27·69	28·36	28·97	29·33	29·74	30·06	30·51	30·82	34·33
E.M.F. in volts . . .	'6163	'6287	'6396	'6527	'6651	'6911	'7985	'8455	'8633	'9046
$\bar{h}_H$ . . .	6·199	6·405	6·586	6·804	7·011	7·443	9·163	9·810	10·04	10·70
$k_3 \times 10^6$ . . .	1·28	1·30	1·32	1·37	1·34	—	—	—	—	—

TABLE VIIIa.—THE DISSOCIATION CONSTANTS OF CITRIC ACID.

C.c. of NaOH	$\left\{ \begin{array}{l} 1·95 \\ 12·39 \\ 22·64 \\ 25·53 \end{array} \right.$	$\left\{ \begin{array}{l} 5·66 \\ 15·48 \\ 26·7 \\ 27·69 \end{array} \right.$	$\left\{ \begin{array}{l} 6·90 \\ 16·90 \\ 27·69 \\ 28·97 \end{array} \right.$	$\left\{ \begin{array}{l} 8·43 \\ 18·51 \\ 9·26 \\ 9·26 \end{array} \right.$	$\left\{ \begin{array}{l} 12·39 \\ 28·7 \\ 28·7 \\ 28·97 \end{array} \right.$	$\left\{ \begin{array}{l} 16·90 \\ 6·00 \\ 9·29 \\ 9·29 \end{array} \right.$	$\left\{ \begin{array}{l} 16·90 \\ 8·43 \\ 9·21 \\ 9·21 \end{array} \right.$	$\left\{ \begin{array}{l} 15·48 \\ 1·95 \\ 9·17 \\ 9·17 \end{array} \right.$
$k_1 \times 10^4$ . . .	9·13	9·22	9·17	9·26	9·26	9·26	9·29	9·29
$k_2 \times 10^6$ . . .	2·78	2·54	2·81	2·66	2·66	2·65	2·69	2·73
$k_3 \times 10^6$ . . .	1·37	1·36	1·36	1·35	1·21	1·38	1·35	1·39

For a tribasic acid, we have from (10) and (11)

$$a_1 = \frac{K_2 K_3 / h^2 + K_2 / h + 1 + h / K_2}{I}; \quad a_2 = \frac{K_3 / h + 1 + h / K_2 + h^2 / K_1 K_2}{I};$$

$$a_3 = \frac{1 + h / K_3 + h^2 / K_2 K_3 + h^3 / K_1 K_2 K_3}{I}; \quad \rho = \frac{1 + K_1 / h + K_1 K_2 / h^2 + K_1 K_2 K_3 / h^3}{I} \quad (20)$$

Fig. 4 shows graphically the relationship between the ionic equilibria in solutions of tricarballylic acid (which may be taken as typical of the series) and the observed hydron concentration.

The maximal concentrations of primary and secondary ions are given by

$$a_1 (\text{max}) = \frac{1}{I} + \frac{K_3 / K_1 + \sqrt{K_2 / K_1} + \sqrt{K_1 / K_2}}{\sqrt{K_2 / K_1} + \sqrt{K_1 / K_2}}$$

$$\text{and } a_2 (\text{max}) = \frac{1}{I} + \frac{K_3 / K_2 + K_3 / K_1}{\sqrt{K_3 / K_2} + \sqrt{K_3 / K_1}}.$$

The positions of the two maxima on the pH axis are defined by the respective relationships  $h^3 = K_1 K_2 (2 K_3 + h)$  and  $h^3 = K_1 (K_2 K_3 - h^2) / 2$  or approximately  $h = \sqrt{K_1 K_2}$  and  $h = \sqrt{K_2 K_3}$ . It follows that the identities (a) and (b) of Auerbach and Smolczyk hold, not at the points corresponding to the formation of (a)  $B_2HA$  and (b)  $BH_2A$ , but at the points at which the concentrations of (a) secondary (b) primary ions, are

maximal. From the figure it is clear that, at any given point within the useful range of the neutralisation curve, at least two dissociation steps are of significance; this accounts for the lack of agreement between the "constants" of Enklaar, and for the failure of equation (7) to represent satisfactorily the course of ionisation.

### Summary

(1) The methods used by Enklaar and by Auerbach and Smolczyk in computing the dissociation constants of tribasic acids are shown to be based on false assumptions.

(2) The acetate buffer mixtures of Walpole, and the phthalate-NaOH and phosphate-NaOH mixtures of Clark and Lubs, may be formulated in terms of the Debye-Hückel theory of inter-ionic forces.

(3) The value

$$k_a = 1.77 \times 10^{-5}$$

is found to satisfy the neutralisation curve of acetic acid.

(4) The dissociation constants of tricarballylic, camphoronic, and citric acids have been determined: the results are in general agreement with the known effects of substitution on the strength of acids.

(5) New apparatus for potentiometric titration, and a new method of differential titration, are described.

The author wishes to express his indebtedness to the Principal and Head of the Chemical Department for the provision of facilities, and to Dr. J. C. Crocker and Mr. A. Hebdon for the kind interest they have taken in the work. A grant from the Dixon Fund of the University of London is gratefully acknowledged.

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### GENERAL DISCUSSION.

The President said that Dr. Lowry had made some reference to the slow changes in conductivity of solutions containing pseudo-acids. In this connection he (the speaker) had often been puzzled by a paradox which he had observed when working with Professor Hantzsch twenty-six years ago. The scarlet compound of ferric iron with acetylacetone was a co-ordinated

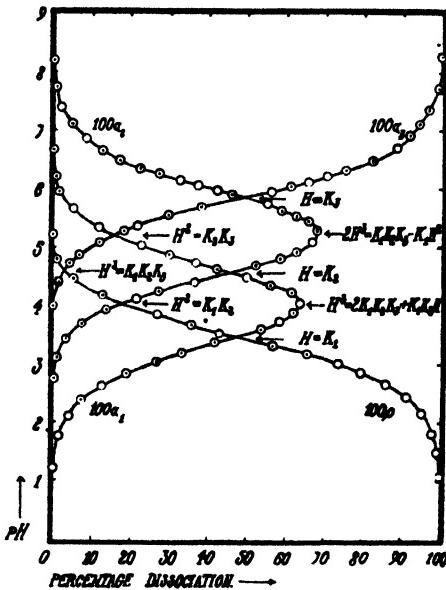


FIG. 4.—Dissociation Curves of Tricarballylic Acid.  
 100<sub>a1</sub> Per cent. of total acid present as primary (H<sub>3</sub>A<sup>+</sup>) ions.  
 100<sub>a2</sub> Per cent. of total acid present as secondary (HA<sup>-</sup>) ions.  
 100<sub>a3</sub> Per cent. of total acid present as tertiary (A<sup>3-</sup>) ions.  
 100<sub>p</sub> Per cent. of total acid present as undisso- ciated acid.

## GENERAL DISCUSSION

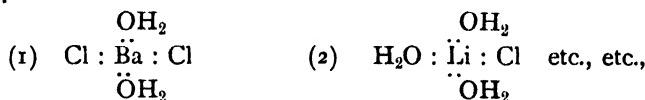
compound and a non-electrolyte. With hydrochloric acid it was slowly converted, through varying shades of purple, due to the gradual introduction of chlorine, into a practically colourless solution of ferric chloride, but a very large excess, some hundred molecules, of the acid was necessary. On the other hand, if dissolved in dry toluene and mixed with a solution of hydrogen chloride in dry toluene, the colour was at once destroyed by the three molecules of hydrogen chloride theoretically required. It might be that this fact had nothing to do with the subject under discussion, but it had seemed to him that it had a bearing on the question, and he would be glad if Dr. Lowry or Dr. Sidgwick could explain it.

He doubted whether any legitimate inference as to the state of mercurous salts in solution could be drawn from the space-lattice of mercurous chloride as determined by X-rays. It was true that the mercury atoms occurred in pairs in the crystal, but so did the chlorine atoms, and it was not clear why that structure should indicate that the mercury atoms would remain coupled on passing from the solid.

He hoped that the valuable paper of Mr. Morton would receive attention. The experimental method was one more application of that most useful laboratory appliance, the thermionic valve, and the author's improvement on Goode's arrangement, by eliminating variations in the high tension battery, should prove of value in measurements of this kind.

**Dr. Flürsheim** said that (a) hydrogen had, according to Bohr, a very small volume compared with carbon. If the hydrogen nucleus were drawn inside the electronic orbits of carbon, then the relative effect of hydrogen on the volume of the resulting compound would be even smaller. But then Sugden's "parachor" theory—which had been repeatedly cited by Professor Lowry in support of his electronic "semi-polar" bond—would be obviously untenable, since it postulated for combined hydrogen a volume over  $3\frac{1}{2}$  times that of carbon, so that carbon, by doubling the number of its outer electrons and absorbing 4 hydrogen nuclei, would acquire a fifteen-fold volume!

(b) Professor Lowry had said that the essential characteristic of weak electrolytes was "that the opposite electric charges of the ions can be neutralised without any violation of the 'octet' rule;" but this was possible also in the case of metallic salts which were strong electrolytes. Using, for instance, Sidgwick's co-ordination theory,  $\text{BaCl}_2$  could be formulated according to (1), and aqueous  $\text{LiCl}$  could complete its Li—Octet as in (2) :—



so that Professor Lowry's criterium did not hold.

(c) He asked what possible connection there could be between the bond which monovalent (and therefore unsaturated)  $\text{Hg}$ -atoms formed with each other, and the nature of the bond between bivalent mercury and an acid radicle?

(d) He said that cyanogen, which was "less hungry" for electrons than chlorine, still had a greater effect than chlorine on the dissociation constants of organic acids and therefore, according to the electronic school, caused a greater "Lewis electron shift" through greater "electron hunger."

(e) Professor Lowry had shown a hydrogen nucleus associated with 4 electrons, notwithstanding that in its period the limiting number was 2, as in helium.

(f) As to the theory of complete dissociation and the assumed complete ionisation of ammonium salts, he had shown, with E. L. Holmes,<sup>1</sup> that diethylbenzylammonium sulphate gave on nitration results which varied with concentration exactly as would be expected if the degree of its ionisation and the degree of its electrolytic dissociation were identical and were a given function of concentration.

**Dr. Ulich (communicated)** said that Professor Lowry's views as to the existence of "weak salts" accorded well with the conclusions to which the more recent work in Professor Walden's Institute led, *viz.*, that on substituted ammonium salts in the dissolved and in the molten condition. In this work, they were dealing with salts which, although in aqueous solution they behaved uniformly as typical strong electrolytes, exhibited notable differences in conductivity in several other solvents even in the somewhat highly diluted condition. Some figures (for  $\Lambda$  values, mostly at 25° C.) should make this clear. (See Tables I. and II.)

In the instances in Table I., where three isomeric cations were taken, the influence of the degree of substitution on the conductivity of the salts was

TABLE I.

Cation.	Water (18° C.).		Methyl Alcohol.		Ethyl Alcohol.	
	Picrate. <sup>2</sup>	Chloride (Bredig).	Chloride. <sup>3</sup>			
	$v = 1000.$	32.	1000.	1000.	100.	
$N(CH_3)_4^+$	62.90	106.0	107.4	41.9	29.2	
$H_2N(C_2H_5)_2^+$	55.28	98.4	97.3	38.8	25.2	
$H_3N(iso\ C_4H_9)_2^+$	54.86	98.9	89.9	35.6	25.1	

TABLE II.

ACETONE AS SOLVENT.<sup>4</sup>

Salt.	$v = 5000.$	500.	100.	Cation.	Picrate Chloride. 1000.	
				$N(C_2H_5)_4I$	$N(C_2H_5)_4Cl$	$N(C_2H_5)_4^+$
$N(C_2H_5)_4I$	189.9	151.6	112.6		148.1	151.6
$N(C_2H_5)_4Cl$	176.2	136	—		155.9	—
$HN(C_2H_5)_3Cl$	—	3	2	$H_2N(C_2H_5)_2^+$	117.3	14.5
$H_2N(C_2H_5)_2Cl$	29.0	11.1	4	$H_3N(iso\ C_4H_9)_2^+$	117.2	14.9
Salt.	Methylene Chloride. <sup>5</sup> $v = 40.$				Chloroform. <sup>6</sup> 2.5.	
$N(C_2H_5)_4Cl$ (strong)	5.84				3.09	
$HN(C_2H_5)_2Cl$	0.236				0.432	
$H_2N(C_2H_5)_2Cl$ (weak)	0.033				—	

<sup>1</sup> *J. Chem. Soc.*, 1926, 1562.<sup>2</sup> *Dissert.*, Birr, Rostock, 1927.<sup>3</sup> Walden, Ulich, and Laun, *Z. physikal. Chem.*, 114, 275, 1925.<sup>4</sup> Walden, Ulich, and Busch, *Z. physikal. Chem.*, 123, 429, 1926.<sup>5</sup> Walden, *Leitvermögen der Lösungen*, Leipzig, 1924, II, 326, 330.

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small. Substituted ammonium salts of all types behaved uniformly as strong salts. One could designate these solvents as *levelling* solvents (of this type also were several hydroxyl free solvents such as  $\text{NH}_3$ ,  $\text{SbCl}_3$ , etc.).

On the other hand, there was another large group of solvents which, on account of the very different kind of behaviour of salts dissolved in them, might be called *discriminating* solvents. The examples in Table II. should illustrate their behaviour.

In the solvents of Table II. the quaternary ammonium salts behaved as strong, and the lesser substituted ones as weak salts.<sup>6</sup>

The anion also influenced the strength of the salts and thus the picrates were the strongest, the perchlorates, iodides, and rhodanides somewhat weaker, and the chlorides weakest. One could, therefore, put together, e.g., the 1, 2 or 3 substituted ammonium picrates with the 4 substituted ammonium chlorides as "medium strength" salts.

The salts behaved in the molten condition in just the same way as in differentiating solvents.<sup>7</sup> Isomeric substituted ammonium picrates of molecular weight 344-386 (with 7-10  $\text{CH}_2$  groups) had at 150° C. the following  $\Delta$  values (Table III.).

TABLE III.  
AMMONIUM PICRATES (MELTED).

Cation.	$\Delta_{150}$ .	$(\Delta\eta)_{150}$
Monosubstituted . . . . .	0·85 - 0·7	0·25 - 0·22
Disubstituted . . . . .	2·2 - 1·3	0·24 - 0·18
Trisubstituted . . . . .	1·7 - 1·2	0·12 - 0·10
Tetrasubstituted . . . . .	5·8 - 5·2	0·52 - 0·47

As to the  $\Delta\eta$  values ( $\eta$  = viscosity) given in column three it could be assumed that the influence of the different ionic mobilities was practically eliminated and that they had an approximate relationship to the ionic concentration just as in the case of the  $\Delta$  values in solution given in the previous tables. Of course, Stokes' law ( $\Delta\eta = \text{constant}$ ) was not obeyed by these salts in the molten state, since  $\Delta\eta$  dropped with the temperature; however, the values apparently approached at 200° C. and upwards a constant value which, for the *strong* quaternary salts, was about 70 to 80 per cent. of the normal value for solutions at infinite dilution ( $\Delta\eta = 0·57 - 0·52$ ). Having in view the high ionic concentration and the strong interionic forces resulting therefrom, such a value was quite compatible with the assumption of *complete dissociation of these strong salts when melted*. On the other hand the (weak) salts of lesser degree of substitution, whose  $\Delta\eta$  might be even as large as that of the quaternary salts (completely dissociated), obviously were only to a small extent dissociated into free ions (about 10 to 50 per cent.).

The lower conductivity of the weak salts in solution and in the molten condition could then, according to considerations of the theory of valency, have two causes, (1) *associated complex ions* (as postulated by Bjerrum), which consisted of essentially fixed ions, might exist; (2) *truly undissociated*

\* It was shown in *Z. physikal. Chem.*, 123, 462, that the lower conductivity of the weak salts is unlikely to be due to splitting up into acid and amine under the influence of the solvent.

<sup>7</sup> Walden, Ulich, and Birr, *Z. physikal. Chem.*, in press.

molecules might come into question, in which one could represent the individuals either, with Lowry, as linked by *non-polar* bonds or with Fajans as *strongly deformed ions*.

Conductivity measurements did not permit decision between these two possibilities, although other methods such as the measurement of dielectric constants (*DC*) were useful.

Their measurements showed that the strong salts caused in dilute solutions a decrease and in concentrated solutions an increase of *DC* relative to that of the solvent (whereby the range of the "diluted" solution expanded with increasing *DC* of the solvent to even greater concentration so that the behaviour of the "concentrated" solutions could only be ascertained in lower *DC* mediums by their measurements). Solutions of weak salts showed only very slight alteration of *DC* in both cases. The examples in Table IV. in which were tabulated the alteration of *DC* relative to that of the pure solvent taken as unity, would make this clear.

TABLE IV.<sup>8</sup>

## DILUTE SOLUTIONS.

Cation.	Acetone, $\nu = 500$ .		Benzonitrile, $\nu = 500$ .	
	Chloride.	Picrate.	Chloride.	Picrate.
$N(C_2H_5)_4$ (strong) . . .	- 0.171	- 0.165	—	- 0.076
$HN(C_2H_5)_3$	- 0.002	—	+ 0.020	—
$H_2N(C_2H_5)_2$	- 0.010	- 0.107	+ 0.013	- 0.020
$H_3NC_4H_9$	- 0.008	- 0.102	—	—

## CONCENTRATED SOLUTIONS.

Chloroform.				
Salt.	$\nu = 100$ .	20.		
$N(C_2H_5)_4I$ (strong) . . .	+ 0.089	+ 0.38		
$H_2N(C_2H_5)_2Cl$ (weak) . . .	$\pm 0.00$	$\pm 0.00$		

The reason for the decrease of *DC* was, according to Debye and Hückel<sup>9</sup> the polarisation of the solvent molecule by free ions; the cause of the increase was the appearance of dissolved particles with high dipole moments. As such the so-called associated complex ions came into consideration since unpolar "undissociated molecules" or molecules consisting of highly deformed ions would not render likely the development of large dipole moments.

The small variations in *DC* which were displayed by weak salts indicated also that the non-conducting particles which existed in great proportion in their solutions were not associated complex ions but undissociated molecules.

This was made still more clear by optical experiments (unpublished) which showed that the depth of colour of solutions of weak picrates in differentiating solvents was very much less than that of strong picrates of equal concentration. Since one might well assume that complex ions are little distinguished, but that the undissociated molecules with their varied

<sup>8</sup> Walden, Ulich, and Werner, *Z. physikal. Chem.*, 116, 261, 1925; Walden and Werner, *ibid.*, 124, 405, 1926.

<sup>9</sup> *Physikal. Z.*, 24, 205, 1923.

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electron shells are strongly distinguished from the free ions in regard to light adsorption, one was led to the conclusion that in the case of weak salts the existence of undissociated molecules was characteristic.

Professor Lowry's interesting paper showed that these considerations were valid not only for the above-mentioned salts with organic cations but also came into question for inorganic salts. In this category were included, e.g., the halogenides of Zn, Cd, etc., which when dissolved in water behaved unlike weak electrolytes but in "differentiating" media approached in their conductivity phenomena to the behaviour of the weak ammonium salts.

**Professor K. Fajans** (*communicated*) said that the existence of weak electrolytes showed, besides other facts, that one must assume many transitional states between the idealised extreme of a molecule built up of rigid ions and the case of a completely non-polar molecule. If one started with free ions, one could picture these transitions as a deformation of the electron shells of the anion by the cation, whereby those electrons of the anion which are pulled over to the cation became common to both atoms. Since, however, the degree of this displacement was different in different cases, it was not sufficient to distinguish only between the two linkage-types of the completely ionised linkage and the covalent linkage, for the respective shares of the two atoms in the common parts of the electron shells could in principle assume all values between 0 and  $\frac{1}{2}$ .<sup>10</sup> Thus the fact mentioned by Professor Lowry, that  $HgCl_2$  is a weak electrolyte whereas  $Hg(ClO_4)_2$  is a strong one, was quite incomprehensible from the standpoint of the usual electronic theory of valency. The outermost electron shell of  $Hg^{++}$ , composed of 18 electrons, is complete, and the octet of  $Cl^-$  is no less complete than that of the O in  $ClO_4^-$ . From the standpoint of the deformation theory the behaviour of these salts was explained immediately. The cations with 18 outer electrons have a strong electron affinity and exercise a correspondingly great deforming action upon anions. But the  $Cl^-$  ion (refractivity 9.00) is much more deformable than the  $ClO_4^-$  ion the refractivity per O octet in which has a value of but 3.33. Therefore the anion in  $HgCl_2$  is much more strongly deformed than in  $Hg(ClO_4)_2$ , and the former compound approximates in its behaviour to that of a non-polar non-electrolyte (*cf.* among other things also its volatility), whereas the perchlorate is a strong electrolyte. The  $NO_3^-$  ion in deformability lies between  $Cl^-$  and  $ClO_4^-$ , and the dissociability of  $Hg(NO_3)_2$  lies also between those of the two other salts.  $CdCl_2$ ,  $CdBr_2$ ,  $CdI_2$  also are incompletely dissociated, and, as the following figures for 25° C. show, the undissociated fraction increases in the order given, which is that of increasing deformability of the halogen ion:

	$CdCl_2$	$CdBr_2$	$CdI_2$
$\Lambda_8 : \Lambda_{4096}$	0.34	0.30	0.21

One could just as easily, from the standpoint of the deformation idea, interpret a fact alluded to as inexplicable by Dr. N. V. Sidgwick<sup>11</sup> in his very interesting lecture on the electronic theory of co-ordination compounds: HF tends towards polymerisation, whereas HCl does not. Now  $F^-$  (refractivity 2.5) is much less deformable than  $Cl^-$ . Therefore upon union with the H nucleus the mutual polarity of the two ions will remain more strongly pronounced in HF than in HCl: the former gives rise to a stronger dipole and consequently polymerises to a greater extent than the latter.

<sup>10</sup> Cf. *Trans. Farad. Soc.*, 1927, 23, 357, 708.

<sup>11</sup> British Assoc., Leeds, 1927.

**Professor Lowry** said that the paper was not intended to introduce any novel theory, but merely to indicate the existence of certain regions within which Arrhenius' theory of reversible ionisation could still be maintained, in face of the inroads that had been made upon it by the more recent theory of complete ionisation.

1. In reply to the President he said that: (a) The curious behaviour of ferric acetyl-acetonate towards hydrogen chloride suggested that the complex will not interact directly with hydrated *ions*, but is decomposed by *molecules* of hydrogen chloride; an analogy was found in the fact that the mutarotation of beryllium benzoyl camphor is catalysed by *chloroform*, which forms a molecular compound with the beryllium salt.

(b) The ionic aggregates of a binary electrolyte might have the structure of zinc blende, of sodium chloride, or of caesium chloride, where each atom was surrounded by 4, 6, or 8 atoms of opposite sign; but the structure of mercurous chloride could only be interpreted rationally on the assumption that the crystals are aggregates of molecules; this was confirmed by the cleavage of the crystals, as well as by their unusual crystal-symmetry.

2. In reply to points raised by Dr. Flursheim: (a) The electronic orbits round the nucleus of a carbon atom would not have the same size as those of binuclear orbits surrounding both carbon and hydrogen; the extent of the expansion resulting from combination of carbon and hydrogen could not be predicted, but might be fifteen-fold or twenty-fold if that is the ratio given by the experimental data.

(b) The ionisation of lithium and barium chlorides would obviously be reversible if the co-ordination compounds formulated by Flursheim were actually formed; but the salts would not behave as weak electrolytes unless the proportion of these non-ionised complexes were comparable with that of the free ions.

(c) There was no clear evidence for the real existence of "monovalent" mercury, since even in the mercurous salts the metal is usually bivalent. It was, however, of interest to observe that, if  $n$  were the number of electrons in an atom of mercury vapour (which was obviously a stable configuration), the mercuric ion  $Hg^{++}$  had a stable configuration with  $n - 2$  electrons; the mercurous ion, on the other hand, did not appear to exist as  $Hg^+$  with  $n - 1$  electrons, but only as  $Hg-Hg$ , with  $n$  electrons round each nucleus, exactly as in the vapour, whilst in the chain-molecule of calomel the number was increased to  $n + 2$ . These numbers showed that the "octet" rule is no longer valid in the case of mercury, although the duplet rule still held good in the sense that all the increments and decrements were of pairs of electrons.

(e) The problem of bivalent hydrogen had been considered fully by Sidgwick who assigned to this element a maximum co-ordination number of 2; this meant that in its co-ordination-compounds the nucleus can be enveloped by four electrons instead of two. The reasons for this view were given in Sidgwick's published papers.<sup>12</sup>

(d) and (f) These paragraphs referred to the problem of aromatic substitution, and involved considerations which were far too polemical to be admitted as evidence for or against the theories of reversible and complete ionisation.

3. In reply to a question by Professor Porter as to the methods of dis-

<sup>12</sup> *Trans. Far. Soc.*, 1923, 19, 469; *J.C.S.*, 1924, 125, 532; cf. "The Electronic Theory of Valency," p. 152.

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criminating between complete and reversible ionisation, Professor Lowry said that the most valuable guide was the X-ray analysis of the crystals. If these were mere aggregates of ions, it was probable that ionisation was also complete in solution. Another valuable clue was found in the colour of the material. Thus, if the chloride of a metal is colourless and the iodide is coloured, the iodine could not be in the form of a colourless iodide ion, but must have formed some sort of a molecule, e.g., by direct union with the metal. The colour of the iodides of mercury therefore confirmed the conclusion that these salts form covalent molecules, and are not "completely ionised."

4. In reply to Dr. Ulich, Professor Lowry said that the contrast between the quaternary halides and those still containing unsubstituted hydrogen in the cation indicated that, both in the fused state and in "discriminating" solvents, real molecules were formed, corresponding with the real molecules which must be postulated in order to account for the weakness of the primary, secondary, and tertiary bases in water.<sup>13</sup> In both cases the relative weakness of the electrolyte depended on the presence of hydrogen linked directly to nitrogen and could be accounted for by the bivalence of this element, as in the formulae  $\text{NR}_3\text{H}.\text{OH}$ ,  $\text{NR}_3\text{H}.\text{Cl}$  and  $\text{NR}_3\text{H}.\text{I}$ .<sup>14</sup>

5. In reply to Professor Fajans he said that sharp distinction between covalence and electrovalence could be maintained if it were supposed that a shared electron moves in a binuclear orbit and occupies one of the limited number of quantised orbits around each nucleus, whilst in a completely ionised aggregate each electron moves in an orbit round one nucleus only. Since, however, a binuclear orbit need not be related symmetrically to the two nuclei, there was plenty of room for the development of an electrical moment in a molecule which is definitely covalent; and conversely the orbits of an ionic doublet might be distorted without becoming binuclear.

<sup>13</sup> Moore and Winmill, *J.C.S.*, 1912, 101, 1635.

<sup>14</sup> Compare Latimer and Rodebush, *J. Amer. Chem. Soc.*, 1920, 42, 1419.

## SOLVATION OF THE DISPERSE PHASE IN JELLIES

By H. GAUNT AND FRANCIS L. USHER.

*Received 29th September, 1927.*

Although it has been generally assumed that the power of gelatinisation of a sol is closely related to the solvation of the disperse phase, the evidence for this view is at present circumstantial, and consists mainly in the observation that typically lyophobic substances—those in which solvation may reasonably be supposed to be absent—do not form jellies. On the other hand, the comparatively slight resistance offered to the diffusion of a crystalline solute by increasing proportions of gelatin in a gelatin jelly<sup>1</sup> indicates that the micellæ may be very little, if at all, hydrated, whilst the successful preparation of jellies of a number of simple metallic oxides and salts suggests the possibility of inducing bodies usually regarded as lyophobic to gelatinise under suitable conditions. The authors have attempted to secure some evidence for or against solvation of a more direct character than that hitherto available, by measuring the change in the con-

<sup>1</sup> Stiles and Adair, *Biochem. J.* (1921), 16, 620.

centration of an indifferent solute caused by gelatinised silicic acid, on the assumption that, if hydration of the micellae occurs, the proportion of the reference substance in the intermicellar liquid will be increased to an extent depending on the hydration. This method has already been used for a similar purpose by McBain and Jenkins<sup>2</sup> in the case of some soap solutions, and is a variation of one previously employed by Philip and Bramley<sup>3</sup> in examining the hydration of crystalline solutes and ions.

### Experimental.

It is necessary that the reference substance used should be chemically indifferent to the micellar material, not appreciably adsorbed by it, and capable of accurate estimation by a volumetric method (the quantities involved being too small for accurate gravimetric analysis). The choice is thus very limited, and of the six substances tried, *viz.*, sulphuric, nitric, oxalic and arsenious acids, chloride, and iodide, only the first two proved entirely satisfactory. It was found that arsenious acid was adsorbed so strongly—probably on account of its amphoteric character—as to reduce the calculated hydration to a negative quantity. It is probable that the simpler acids, sulphuric and nitric, were not appreciably adsorbed, since the results were not visibly affected by varying the concentration; and it is evident from the work of Mukherjee<sup>4</sup> and of Joseph and Hancock<sup>5</sup> that the adsorption of simple inorganic acids by silica gel is either undetectable or so small as to be of no significance.

The procedure was to pour a solution of water glass into an excess of acid solution containing the reference substance, the quantities and composition of the liquids being so arranged that the resulting mixture remained homogeneous and liquid during a time long enough for a sample to be taken, weighed, and diluted. The remaining liquid was then placed in a Jena glass flask which was closed with a paraffined cork, sealed with paraffin wax, and set aside. Gelatinisation took place in from 2 to 36 hours, after which the jelly was left to undergo syneresis for from 3 to 6 weeks. The intermicellar liquid can be obtained from a jelly (1) by ultrafiltration (2) by electro-osmosis, or (3) by syneresis. The first method, in the case of an emulsoid like silicic acid, involves the use of high pressures and severe mechanical disturbance of the jelly, whilst the second can only be used when the concentration of electrolytes is very small. On the other hand the natural process of syneresis, although slow, furnishes a sufficient quantity of liquid with the least possible mechanical or chemical disturbance of the system. In these experiments the liquid which had exuded from the jellies in the course of a few weeks was poured into a weighing bottle, weighed, and diluted to a known volume, the diluted liquid being then analysed volumetrically by means of the same solution that was used for the sample of the original liquid before its gelatinisation. The results were calculated on the assumption that any water forming part of the micellar structure is incapable of holding the reference substance in solution. In this case, if  $a$  = weight of the original sample,

$b$  = weight of liquid expressed during syneresis,

$v_1$  = titration value (in terms of the reference substance) of ( $a$ ),

$v_2$  = titration value of ( $b$ ), and

$c$  = weight of  $\text{SiO}_2$  in ( $a$ ),

<sup>2</sup> McBain and Jenkins, *J. Chem. Soc.* (1922), 121, 2336.

<sup>3</sup> Philip and Bramley, *J. Chem. Soc.* (1915), 107, 377, 1831.

<sup>4</sup> Mukherjee *et al.*, *J. Chem. Soc.* (1926), 3023.

<sup>5</sup> Joseph and Hancock, *J. Chem. Soc.* (1923), 123, 2022.

the number of molecules of water associated with one molecule of  $\text{SiO}_2$  is

$$R = \frac{10}{3} \left( \frac{a}{c} - \frac{b\gamma_1}{c\gamma_2} - 1 \right).$$

A few experiments were made with precipitated silicic acid prepared by adding acid to a solution of sodium silicate in presence of chloride or oxalate as reference substance, but the results were not very satisfactory owing to the persistent inclusion of liquid in the gelatinous lumps. By breaking up the latter as completely as possible and allowing the broken material to remain in contact with the liquid for several days values of the ratio were obtained which, although showing poor agreement amongst themselves, indicate definitely the occurrence of hydration of approximately the same magnitude as in the jellies. Similar measurements were made with ferric and aluminium hydroxides. The results are given in the following Table:—

#### I. Silicic Acid Jellies.

Percentage $\text{SiO}_2$ in Jelly.	Nature of Reference Substance.	Conc. of Dissolved Electrolytes in Moles per 1000 gms.	Calculated Molecular Hydration ( $\text{H}_2\text{O} \cdot \text{SiO}_2$ ).
3.7	$\text{HNO}_3$ ( $\text{Cl}'$ )	3.6	0.82 (1.21)
4.4	$\text{H}_2\text{SO}_4$ ( $\text{C}_2\text{O}_4''$ )	1.4	0.93 (1.20)
4.5	$\text{HNO}_3$ ( $\text{Cl}'$ )	3.4	0.83 (0.99)
4.55	"	3.4	0.84 (1.11)
4.6	$\text{H}_2\text{SO}_4$ ( $\text{Cl}'$ )	1.4	1.11 (0.84)
4.7	$\text{H}_2\text{SO}_4$ ( $\text{C}_2\text{O}_4''$ )	1.3	0.81 (1.05)
4.75	"	1.3	0.75
5.75	"	1.2	1.15
5.9	"	1.2	1.18
6.15	"	1.2	1.23
6.2	"	1.2	1.17
6.45	"	1.6	0.94
7.1	"	1.2	1.16
7.5	"	1.4	1.19
7.6	"	1.4	1.18
9.3	"	1.4	1.39

#### II. Precipitated Silicic Acid.

$$\text{H}_2\text{O} : \text{SiO}_2 = 2.13, 1.23, 0.33, 1.96, 1.73, 1.50. \quad \text{Mean, } 1.5.$$

#### III. Precipitated Ferric Hydroxide.

$$\text{H}_2\text{O} : \text{Fe}_2\text{O}_3 = 2.7, 2.3, 4.0, 2.9. \quad \text{Mean, } 3.0.$$

#### IV. Precipitated Aluminium Hydroxide.

$$\text{H}_2\text{O} : \text{Al}_2\text{O}_3 = 7.0, 5.8, 5.5, 6.2. \quad \text{Mean, } 6.1.$$

*Accuracy of the Results.*—One essential condition of obtaining trustworthy results, *viz.*, the determination of the reference substance in a proper sample of the intermicellar liquid, was probably not strictly fulfilled in the experiments in which precipitation occurred immediately on mixing the two solutions, since even after a long time the distribution of the reference substance between the free (filterable) liquid and that enmeshed in the precipitate may not be quite uniform. The poor agreement of the figures for precipitated silicic acid, ferric and aluminium hydroxides is probably due to this cause, and the values therefore give only a rough idea of the hydration. On the other hand, the silicic acid jellies were perfectly

homogeneous since gelatinisation never occurred earlier than 2 hours after mixing, and the values obtained are subject only to the ordinary errors of analysis. The most serious of these is an error in the titration values, since on the average a difference of 0·1 c.c. in one of the titration values corresponds to a difference of about 27 per cent. in the calculated ratio  $H_2O = SiO_2$ . All the measuring vessels used were carefully calibrated, and not less than three titrations—each involving about 30 c.c.—were carried out, which usually agreed within 0·02 c.c., the maximum divergence being 0·05 c.c. in one case only. This is true of the experiments in which acid (sulphuric or nitric) was the reference substance, but the same accuracy could not be attained in the case of any of the other substances tried. The standard alkali was in all cases added from the burette, using methyl red as the indicator. A correction was necessary for the silicic acid present in the original mixture, and was ascertained by dissolving a weighed quantity of carefully washed silica in standard sodium hydroxide, acidifying this solution with a known excess of standard acid, and titrating the resulting liquid with standard alkali, so as to reproduce very closely the actual experimental conditions as regards volume of liquid and concentration of salts. The correction amounted to 1·60 c.c. decinormal alkali per 1 gm. of  $SiO_2$ , and was in each case subtracted from the titration value of the original mixture. A further correction was necessary if any silica was found in the liquid expressed from the jellies by syneresis, but this was generally absent, the largest quantity found being 0·16 per cent., or about 1/60 of the total amount present.

### Discussion.

The final mean of the ratios from the sixteen experiments with silicic acid jelly, using acid as the reference substance, is  $1\cdot04 \pm 0\cdot03$ , a result which, considered by itself, suggests a possible chemical mechanism of gelatinisation; for if the process is dependent on the formation of fibrils consisting of long chains of molecules serving to enmesh the intermicellar liquid, it is evident that such chains might be formed from metasilicic acid, in which case the ratio  $H_2O : SiO_2$  would the more closely approach unity as the length of the chain designated by



increased. In view of the many circumstances which indicate a connection between gelatinisation and the formation of long chains, it appeared to be of interest to examine one of the probable consequences of this theory, according to which solvation may not be a necessary condition of gelatinisation. Thus the oxide of any element having a valency greater than 1 can be formulated as a chain of indefinite length, a single molecule of water only being needed to keep the chain open by providing terminal hydroxyl groups; and it is known that jellies can be prepared from cupric, ferric, stannic, and other oxides. If, however, this explanation is valid, the substitution of sulphur for oxygen should not affect the capacity for chain formation, and some of the resulting compounds would belong to a class distinguished by lyophobic properties. Accordingly jellies were prepared from stannic and cupric oxides and from the acetone compound of mercuric oxide, and pieces of them were left in a large vessel filled with hydrogen sulphide. After several days the change from oxide to sulphide was apparently complete, but was in every case accompanied by the destruction of the jelly structure. In a few instances the approximate

shape of the original piece of jelly was maintained, but the resulting material was a semi-rigid mud possessing no shearing elasticity. A further attempt was made to prepare jellies of stannic and arsenious sulphides by dissolving the washed precipitates in the minimum quantity of alkali and mixing the solutions with a solution of methyl oxalate in quantity sufficient to provide an equivalent amount of acid. The ester was gradually hydrolysed, liberating the sulphides slowly and uniformly, but in each case a thick mud was the nearest approach to jelly formation.

The negative results just described fail to support the chemical chain hypothesis in the particular cases examined, and it seems probable that the close approach of the ratio  $H_2O : SiO_2$  to unity is accidental and devoid of chemical significance. Moreover, the much larger ratios found for ferric and aluminium oxides do not favour a chemical explanation.

The figures calculated for the molecular hydration of the substances examined are of course subject to the same uncertainty of interpretation as in other cases of depression of solubility; but it is clear that if they do not possess the significance assigned to them here, they show that certain insoluble substances in the condition of a rigid phase can diminish the solvent power of water in the same way and to about the same extent as do a number of soluble bodies such as sugars and various salts,<sup>3</sup> as well as some colloidal substances in a mobile state.<sup>6</sup>

<sup>3</sup> Findlay and Creighton, *J. Chem. Soc.* (1910), **97**, 536; Findlay and Shen, *J. Chem. Soc.* (1912), **101**, 1459; Findlay and Williams, *J. Chem. Soc.* (1913), **103**, 636; Findlay and Howell, *J. Chem. Soc.* (1914), **105**, 291; (1915), **107**, 282.

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#### ADSORPTION IV.—ADSORPTION BY COCONUT CHARCOAL FROM BINARY MIXTURES OF SATURATED VAPOURS. THE SYSTEMS METHYL ALCOHOL-BENZENE, ETHYL ALCOHOL-BENZENE, N-PROPYL ALCOHOL-BENZENE, AND N-BUTYL ALCOHOL-BENZENE.

By F. G. TRYHORN AND W. F. WYATT.

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It has been shown in previous communications<sup>1</sup> that the adsorption of a binary saturated vapour mixture by charcoal occurs in three well-defined stages. The first is the adsorption of the two components in a constant ratio which is close to that existing in the saturated vapour phase. This process is complete in a few hours and, in the systems previously examined, terminates quite sharply. Reasons have been advanced for regarding the end of this stage as coincident with the condensation of the adsorbed vapour to the liquid phase. In the second stage a somewhat slow change occurs in the composition of the adsorbed phase. This change may occur without much alteration in the total number of adsorbed molecules, and entails the partial replacement of one component by the other. At the end of this stage the composition of the adsorbed phase approaches, although it is

<sup>1</sup> Tryhorn and Wyatt, *Trans. Far. Soc.*, 1926, **22**, 139.

never coincident with, that of the bulk liquid in contact with the saturated vapour mixture. It has been suggested that the selective adsorption powers of the charcoal manifest themselves during this stage, and that the extent of this selective adsorption is measured by the difference between the composition of the adsorbed phase at the end of this stage and that of the bulk liquid remaining in contact with the vapour mixture.

The third stage of adsorption is indefinitely prolonged and consists in an isothermal distillation of the bulk liquid into the interstitial spaces of the charcoal. Theoretically this will continue until the radius of curvature of the liquid surfaces in these spaces becomes infinite.

To confirm the existence of these three stages of adsorption and to investigate further the nature of the second stage, an examination has been made of the adsorption by coconut charcoal from mixtures of benzene with the first four members of the normal aliphatic alcohol series. The results for the system ethyl alcohol-benzene have already been communicated.

### Experimental.

The alcohols were purified and carefully dried by standard methods. The benzene was distilled over potassium permanganate and subsequently frozen out thrice. The charcoal used in the series methyl alcohol-benzene and propyl alcohol-benzene was the remainder of the batch prepared for the earlier work. It was necessary to prepare a fresh batch of charcoal for the system butyl alcohol-benzene. The charcoal previously prepared was a portion of a large batch of coconut shells which had been charred under sand in a gas-fired annealing furnace, and was activated before use by heating to 600° C. for two hours. The new sample of charcoal was a further portion of the large batch of charred shell, but was separately activated under conditions as close as possible to those maintained during the activation of the first batch.

In the determination of the adsorption curves for the system butyl alcohol-benzene, these two charcoal preparations were used alternately in order to test the reproducibility of the adsorbent. That the reproducibility was satisfactory was shown by the fact that the points obtained lay on smooth curves irrespective of the sample of charcoal used.

The experimental methods of measuring the adsorption curves and the compositions of the vapours in equilibrium with the binary liquid mixtures were those previously described. The liquid mixture placed in the adsorption tubes at the beginning of an experiment is referred to as the bulk liquid mixture, and the liquid and vapour present in the tube at the end of any experiment are described as the bulk equilibrium liquid and the equilibrium vapour respectively.

### Results and Discussion.

The essential results for the four systems are shown in Fig. 1. In these diagrams, which are selected to show principally the second stage of the adsorption process, the composition of the adsorbate is represented as a function of the total amount of the adsorbed phase, expressed in moles per gram of adsorbent. In every case the first and third stages of adsorption were found to be represented by straight lines, and the individuality of the adsorption process for a given mixture may therefore be illustrated by reference to the second stage alone.

*The First Stage.*—It has been mentioned above that the first stage is considered to consist in the packing of molecules, still in the vapour state,

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into the pores of the charcoal. The proportions in which the components of a binary vapour mixture will be adsorbed in this stage will depend primarily on the composition of the vapour, and on the partial pressures

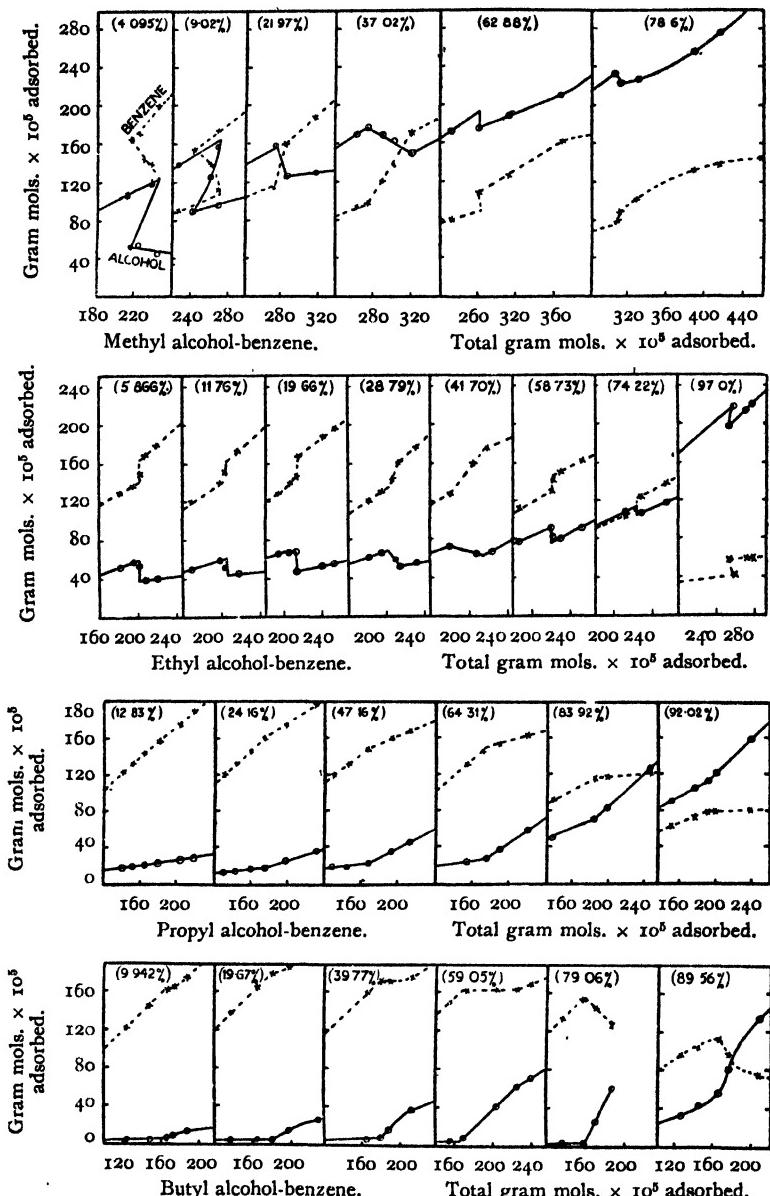


FIG. I.

and the diffusion coefficients of the components. It has been pointed out by Mack<sup>2</sup> that if a porous substance adsorbs vapour molecules as quickly

<sup>2</sup> Mack, *J. Amer. Chem. Soc.*, 1925, 47, 2468.

as they are presented to its surface, the weight of vapour  $g$  taken up in the time  $t$  is given by the expression  $g = DATd/l$ , where  $A$  is the cross-section of the diffusion area,  $D$  the diffusion coefficient, and  $d$  the density of the vapour in gms. per c.c. at the surface of the evaporating liquid. For a binary mixture the ratio of the weights of the two components adsorbed at the time  $t$  becomes  $g_1/g_2 = D_1d_1/D_2d_2$ , where  $D_1$ ,  $D_2$  are the diffusion coefficients, and  $d_1$ ,  $d_2$  the densities of the two components in the vapour phase. This ratio should thus be independent of time, and indeed is found experimentally to be so. This is shown by the straight lines forming the first stage of the adsorption process in Fig. 1. For, although the abscissæ in these figures represent the total number of moles of the adsorbate, they may be regarded as representing implicitly a function of time. At the same time, it must be remembered that adsorption is becoming slower the further it proceeds, and the first stage of the process is therefore not necessarily represented by straight lines when the amounts of the two components adsorbed are plotted against time, as has been done by other observers.<sup>3</sup> Nevertheless, even when results are so plotted the constancy of the above ratio may be seen to persist up to the point at which the curvature changes abruptly at the end of the first stage.

It is not possible to apply Mack's equation quantitatively to the present results owing to lack of knowledge of the true densities and diffusion coefficients of the components of a binary mixture. A rough calculation of the composition of the adsorbed phase may, on the other hand, be made by the use of Langmuir's equation<sup>4</sup>  $\mu = p\sqrt{2\pi MRT}$ , for the number of gram moles  $\mu$  of a gas, of molecular weight  $M$ , which strike each square cm. of a surface per second, at the absolute temperature  $T$ . For a binary mixture the ratio of the numbers of moles of the two components adsorbed becomes  $\mu_1/\mu_2 = p_1\sqrt{M_2}/p_2\sqrt{M_1}$ , provided that the molecules can be adsorbed as rapidly as they reach the adsorbing surface. In the early stages of adsorption we may assume this to be the case. If now  $X_1$  and  $100 - X_1$  are the molecular percentages of the two components in a binary vapour mixture over a liquid mixture of which the total vapour pressure is  $P$ , then, regarding as an approximation the partial pressures of the two components as proportional to their mole fractions in the vapour phase, we may write for these partial pressures  $p_1 = (X_1/100)P$ , and  $p_2 = [(100 - X_1)/100]P$ . The molar ratio in which the two components will be adsorbed then becomes  $\mu_1/\mu_2 = X_1\sqrt{M_2}/(100 - X_1)\sqrt{M_1}$ . Thus  $\mu_1/\mu_2$  may be calculated if the composition of the vapour in contact with the bulk liquid mixture is known. The table shows the calculated and observed values of the adsorbed phases during the first stage for the four series studied.

In the methyl alcohol-benzene, and ethyl alcohol-benzene series the discrepancies between the observed and calculated compositions of the adsorbed phase are not great, when the approximate nature of the calculation is taken into account. In making these calculations it has been assumed that the partial pressure of each component in a binary mixture is proportional to its mole fraction. This is inaccurate, especially in dealing with saturated vapours at temperatures considerably removed from the natural boiling-points of the liquid components. It is noteworthy that in the two latter series, in which the mixed liquids possess considerably higher boiling-points than in the former, the numerical values of the discrepancies

<sup>3</sup> Williams, *J. Soc. Chem. Indus.*, 1924, 43, 97T.

<sup>4</sup> Langmuir, *Trans. Far. Soc.*, 1922, 17, 625.

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System.	Composition of Bulk Equilibrium Mixture. (Molar Per Cent. Alcohol.)		Composition of Adsorbed Phase. (Molar Per Cent. Alcohol.)		Difference Between Observed and Calculated Values.
	Liquid.	Vapour.	Observed.	Calculated.	
Methyl alcohol-benzene	4·7	36·0	50·0	46·7	+ 3·3
	14·7	46·8	60·7	57·9	+ 2·8
	39·0	48·5	57·0	59·5	- 2·5
	53·4	51·7	64·6	64·0	+ 0·6
	81·75	63·75	68·1	73·2	- 5·1
	91·0	73·7	76·1	81·5	- 5·4
Ethyl alcohol-benzene	7·9	19·9	29·1	24·45	+ 4·65
	17·5	26·8	30·2	32·2	- 2·0
	29·0	29·9	33·0	35·7	- 2·7
	41·1	31·3	33·65	37·2	- 3·55
	56·2	34·5	36·3	40·6	- 4·3
	72·6	42·0	41·3	48·6	- 7·3
	85·2	53·2	50·9	59·7	- 8·8
<i>n</i> -Propyl alcohol-benzene	16·4	10·6	12·1	11·9	+ 0·2
	30·8	14·4	9·1	16·0	- 6·91
	56·5	18·5	13·0	20·46	- 7·46
	74·4	20·4	14·75	22·5	- 7·75
	90·9	46·2	37·3	49·3	- 12·0
	96·5	70·0	59·25	72·5	- 13·25
<i>n</i> -Butyl alcohol-benzene	11·1	3·25	3·13	2·85	+ 0·28
	22·3	4·0	3·0	4·1	- 1·1
	44·0	4·5	2·9	4·61	- 1·7
	64·3	5·2	2·41	5·34	- 2·93
	84·8	13·0	1·91	13·3	- 11·39
	94·8	36·0	25·35	36·6	- 11·25
	95·3	39·5	32·9	40·2	- 7·3

are greater. Further, in any one series a change of sign in the divergence occurs and if these divergences are plotted against the molar percentage of the alcohol in the vapour phase from which adsorption has occurred, an S-shaped curve is obtained, indicating zero divergence at some particular point. These zero values occur, for the methyl alcohol series at 51 per cent., for the ethyl alcohol series at 28 per cent., for the propyl alcohol series at 10 per cent., and for the butyl alcohol series in the neighbourhood of 3 per cent. These values agree closely with the compositions of the minimum boiling-point mixtures of these alcohols with benzene, which from the measurements of the composition of the vapours in equilibrium with the liquids have been found to be, at 20° C., 51·5 per cent., 30 per cent., 9·5 per cent., and 2·5 per cent. respectively. This suggests that the above discrepancies may be due to the error introduced in treating the partial vapour pressures of the vapour components as proportional to their mole fractions.

Inasmuch as for a minimum boiling-point mixture the composition of the liquid phase is the same as the composition of the vapour phase, the divergences of the true vapour pressure of each component from the value calculated from the molar percentage composition of the liquid phase may be regarded as equal for these mixtures. Thus, if  $p_1$  and  $p_2$  are the true

partial pressures of the two components, and  $p_1'$ ,  $p_2'$  those calculated from the composition of the vapour, then  $p_1 = k_1 p_1'$ ,  $p_2 = k_2 p_2'$ . For the minimum boiling-point mixture  $k_1 = k_2$ , and thus  $p_1/p_2 = p_1'/p_2'$ . In these circumstances it is obvious that zero discrepancy should be found between the calculated and the observed compositions of the adsorbed phase, if the bulk equilibrium liquid has the composition of the minimum boiling-point mixture. Approximately these conditions have been encountered in the case of the 53·4 per cent. mixture of methyl alcohol and benzene.

Further proof of the close relation between the composition of the adsorbed phase during the first stage, and the form of the vapour pressure curve of the binary system is afforded by a study of the results previously communicated for the system acetone-benzene. If a comparison is made for this series between the experimental values of the composition of the adsorbate and those calculated from Langmuir's equation the change of sign in the discrepancies is absent, and in all cases the calculated values are less (by 0·5 to 4·7 per cent.) than the experimental ones. This is to be anticipated since acetone and benzene do not form a minimum boiling-point mixture.

It may be mentioned here that the present method of studying adsorption appears to offer, by the application of Langmuir's equation, a method of determining indirectly the true, or effective, partial pressures of the components of a binary vapour mixture by a reversal of the above calculation, for systems in which molecular association of the components may be presumed to be negligible or absent.

Additional evidence that this first stage is a purely diffusional process is afforded by a comparison of the times necessary for its completion in the different series. In the methyl alcohol-benzene series the first stage is complete in from 3 to 4 hours; in the ethyl alcohol-benzene series, from 4 to 9·5 hours are necessary, the time increasing with the percentage of alcohol in the mixture; in the propyl alcohol series, the time required is from 18 to 48 hours, while for the butyl alcohol series, from 6 to 24 hours are necessary. The propyl alcohol series is anomalous inasmuch as the second stage is absent, or rather, overlaps the first and third stages. Consequently the above times for this series include part of the second stage, and are greater than the true values. Since, as will be shown later, the numbers of molecules adsorbed at the completion of the first stage do not vary greatly, the time required for the process, if purely diffusional, will vary inversely with the mean value of  $p/\sqrt{M}$  for the system in question. The values of  $p/\sqrt{M}$  for methyl alcohol, benzene, ethyl alcohol, propyl alcohol, and butyl alcohol decrease in that order from 14·4 to 0·59 at 20° C. The increase in the time required for the first stage from system to system is thus parallel with the decrease in the value of the average  $p/\sqrt{M}$  for the mixtures, except in the case of propyl alcohol, to which reference has been made above.

*The Volume of the Adsorbate at the First Break Point.*—Assuming that liquefaction of the adsorbate occurs at the first break point, we can calculate the volume occupied by that adsorbate by dividing the weight of each component at the break point by its density in the liquid state. When this is done the total volume of adsorbate is found to be approximately constant at 0·16 c.c. per gram of charcoal. The mean values for the four systems, methyl alcohol-benzene to butyl alcohol-benzene, are 0·1618, 0·1622, 0·156, and 0·150 c.c. respectively, per gram. of charcoal. The average variation for the various series in a system was about 3 per cent. The mean value

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for the free spaces in a gram of the charcoal, calculated from the four systems, is  $0.1575$  c.c. This confirms the value of  $0.16$  c.c. previously obtained by a more direct method. Since the volume of adsorbate is constant at the first break point, the number of molecules actually present will vary inversely with the molecular volume of the components, and we thus find that in each series, as well as in different systems, slight but regular variations in the number of molecules present at the first break point. The molecular volumes at  $20^\circ\text{C}$ . of the substances methyl alcohol, ethyl alcohol, propyl alcohol, benzene, butyl alcohol, are respectively  $40.6$ ,  $58.3$ ,  $74.6$ ,  $88.7$ , and  $91.4$  c.c.s. Accordingly, we find that the greatest number of molecules is adsorbed at the first break point in the methyl alcohol series, and that within this system, the total number of molecules adsorbed increases as the individual mixtures become richer in methyl alcohol. Numerically the increase is from  $1.50 \times 10^{21}$  to  $1.86 \times 10^{21}$  molecules per gram. of charcoal. In the ethyl alcohol series the corresponding figures are  $1.2 \times 10^{21}$  and  $1.55 \times 10^{21}$ , whilst for the butyl alcohol series the average value falls to  $1.0 \times 10^{21}$  molecules.

In Fig. 2 the numbers of gram mols. of the four alcohols adsorbed at the first break point are plotted against the molar percentages of alcohol in the vapour phase. An interesting point arises from these curves inasmuch as the points at the extremities of the full lines represent the maximum amount of

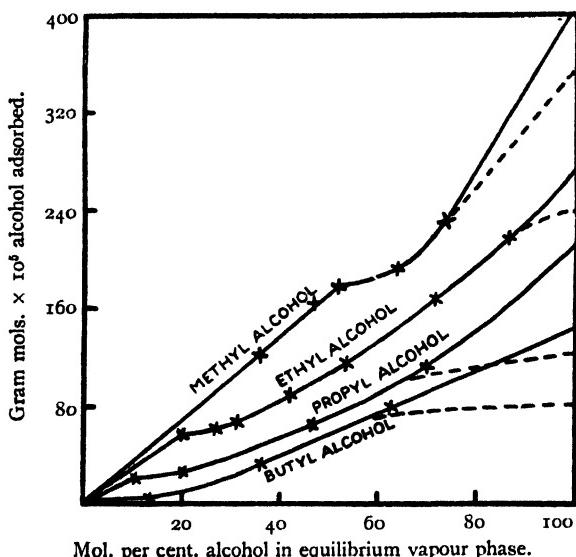


FIG. 2.

the alcohol adsorbable by a gram of charcoal, as determined by the continuous adsorption method for pure vapours described in a previous paper. The points at the 100 per cent. alcohol ends of the dotted curves refer to the break points on the adsorption curves for the pure liquids, and indicate the points at which condensation occurs in the pores of the charcoal when one substance only is present. The maximum values on the same curves represent a complete filling of the charcoal pores, the volumes lying close to the value  $0.16$  c.c. It is evident, therefore, that the appearance of a liquid phase occurs more readily when one substance only is in the pores than when a binary mixture is present. The same rule holds for the benzene, the break point in the adsorption curve for pure benzene occurring at  $120 \times 10^{-5}$  gram mols. per gram of charcoal. When curves for benzene adsorption in the binary mixtures are plotted in a manner similar to that of Fig. 2, it is found that above 55 per cent. the adsorption of the benzene is almost proportional to the molar percentage of benzene in the vapour, the straight line representing such adsorption

terminating at the maximum value for the adsorption of pure benzene. Below about 55 per cent., the adsorption of the benzene is considerably more than proportional to the percentage of benzene in the vapour. It thus appears that in adsorption from a polycomponent system, the tendency to condensation of each component is decreased by the presence of the others. Reference will be made to this point after dealing with the second stage of adsorption.

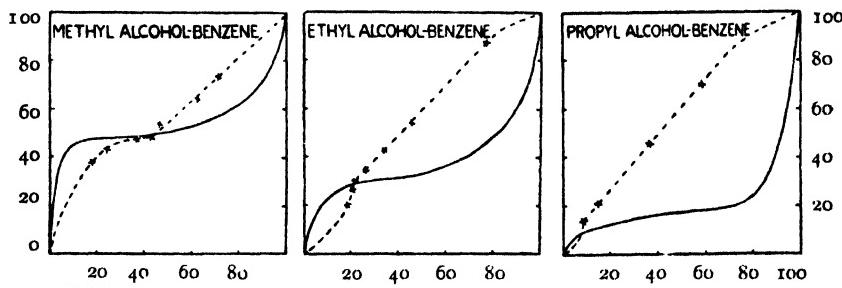
*The Second Stage.*—It is obvious from Fig. 1 that the sharpness and extent of the second stage in the adsorption process varies greatly from system to system. In the methyl alcohol-benzene and ethyl alcohol-benzene systems this stage is extremely sharp and well-defined. In the propyl alcohol-benzene series it is indistinguishable, while in the butyl alcohol-benzene series it becomes more prominent and extensive as the amount of butyl alcohol in the bulk liquid is increased. During this stage in the methyl and ethyl alcohol systems, a change of composition occurs in the adsorbed phase, without much change in either volume or total number of molecules adsorbed, by a process of replacement of alcohol molecules by benzene molecules. In the lower series of the methyl alcohol-benzene system this change is accompanied by a slight decrease in the total number of molecules in the adsorbed phase, owing to the fact that the benzene molecule is considerably larger than the methyl alcohol molecule, and therefore to fill a given pore volume the number of methyl alcohol molecules ejected must be greater than the number of benzene molecules taking their places. In the ethyl alcohol series, where the difference in molecular volume of the components is less marked, replacement occurs practically without change in the total number of adsorbed molecules, except from the mixture containing 95·04 weight per cent. of alcohol, in which case there is a slight decrease in the total number of molecules in the adsorbate during the replacement process. Irregularities were found when the initial liquid mixtures were close to the minimum boiling-point mixtures. In these cases, presumably owing to the high vapour pressure exhibited by such mixtures, and the consequent acceleration of adsorption, the replacement process was synchronous with a steady increase in the number of molecules adsorbed, and there appeared a tendency for this second stage of adsorption to coalesce with the third. This is shown in the curves for mixtures containing 37·02 wt. per cent. of methyl alcohol, and 28·79 and 41·7 wt. per cent. of ethyl alcohol.

In the propyl alcohol-benzene series the above tendency towards coalescence appears to have become complete, for it was not possible to detect any definite second stage. The only evidence of a second stage in this system is in the bunching of points which occurred after the first break point. In the butyl alcohol series the emergence of a definite second stage is clearly shown by reference to the curves for this system in Fig. 1. In no mixture of this series was the second stage as completely masked as in the propyl alcohol series, but as the amount of butyl alcohol in the original liquid increased, the second stage became more marked, involving at first an increase in the number of alcohol molecules while the number of benzene molecules remained practically constant, and then later, as in the curves for mixtures containing 79·06 and 89·56 wt. per cent. of alcohol, a replacement of benzene by alcohol molecules. The replacement in this series is opposite in direction to that in the methyl alcohol and ethyl alcohol series.

The cause of this replacement process is to be found in the effort of the liquid adsorbate, newly formed at the first break point, to come into

equilibrium with the remaining bulk liquid mixture. By reference to Table I. it is possible to see in which direction replacement should occur during the second stage to set up this equilibrium. In the methyl alcohol series, with bulk liquid mixtures containing up to 53·4 molar per cent. of methyl alcohol, the adsorbed phase at the first break point contains more alcohol than the bulk liquid, and therefore to reach the second equilibrium methyl alcohol should be displaced by benzene. This is found experimentally to be the case. But by the same argument, mixtures containing more than 81·75 molar per cent. of methyl alcohol should show the reverse displacement, although experimentally the alcohol is replaced by benzene throughout the series.

In the ethyl alcohol-benzene series an inversion of the direction of replacement should occur between mixtures containing 29·0 and 41·1 molar per cent. of alcohol. Here again no inversion is found, but throughout the series benzene replaces alcohol. In the propyl alcohol-benzene series, no inversion of replacement in the mixtures studied should occur, but propyl alcohol should always replace benzene. In the butyl alcohol-benzene system, in each series butyl alcohol should replace benzene, and this is found to be the case wherever any replacement occurs. In consequence of these discrepancies, a comparison of the compositions of the adsorbate at



Full line curve-comp of bulk equil. liquid. Dotted line curve .....adsorbed phase.

FIG. 3.

the second break points with those of the equilibrium bulk liquids shows that equality of composition is never attained. Now this equality of composition should be reached if the total and partial vapour pressures of a liquid mixture in a pore are the same as those of a bulk liquid mixture, and we are therefore forced to infer that the effect of the so-called selective properties of a charcoal must act in such a direction as to modify the total and partial vapour pressures of adsorbed substances. It must be pointed out here that such action cannot be assigned to the effect of a radius of curvature on the vapour pressures of the components of the adsorbate, for as has been mentioned above, at this stage of adsorption, the pores of the charcoal are full, and the radius of curvature is infinite. The differences in composition between the adsorbate and the bulk liquids at the second break points are shown in Fig. 3. In this diagram the broken lines represent the compositions of the adsorbate at the second break points and the full lines those of the bulk equilibrium liquids, plotted in each case against the compositions of the equilibrium vapours. For the propyl alcohol-benzene system the values of the first break points have been used, since these are coincident with the second break points. The curve for the butyl alcohol system is not shown, owing to the difficulty of determining exactly the end of the second stage as a result of the overlap-

ping of the second and third stages. An attempt was made to calculate the compositions of the adsorbates in this system at the second break points by a method referred to later. The curve so obtained was of a form similar to the experimental ones for the other two series.

The selective action of the charcoal is shown by the areas between the full and broken curves. The decrease in selective adsorption as the minimum boiling-point mixtures are approached is clearly shown, since the full and broken curves cross in each system close to those mixtures. The chief point of interest in this diagram lies in the fact that with bulk mixtures containing more alcohol than the minimum boiling-point mixture, the composition of the adsorbed phase is almost a linear function of the composition of the equilibrium vapour. In each case, however, this linear curve is displaced approximately parallel with the diagonal of the diagram, indicating that the adsorbed phase contains less alcohol than the vapour, but that the deficiency is a constant quantity. The physical significance of this appears to be that the partial vapour pressure of the alcohol in the adsorbate is enhanced in comparison with that of the benzene. This is in agreement with the recent work of Baker, who finds that certain adsorbent substances<sup>5</sup> possess the property of altering the vapour pressures of pure liquids into which they are placed. Charcoal, for example, was found to cause an increase of 12 mms. in the vapour pressure of methyl alcohol at 35° C., and of 2 mms. in that of benzene. It is therefore suggested that the mechanism of selective adsorption in this second stage may be found in the relative changes effected by the charcoal in the partial pressures of the components. Further than this it is not possible to go at present, but whereas Baker suggests that these changes are to be attributed to alterations in the degree of association of the molecules, it is also possible that we are dealing with molecular phase changes of the type suggested by Baly.<sup>6</sup>

These phase changes may conceivably be occasioned by the effect of the force fields which must exist in the charcoal pores on those existing among the molecules of the adsorbed phase. The source of the energy changes between different molecular phases of the adsorbate might then be found in the transfer of quanta of energy between the charcoal surfaces and the adsorbate molecules, the direction of the transference depending on whether the charcoal increases or decreases the vapour pressure of the adsorbent.

It may further be suggested that these energy transfers occur in the infra-red region in the neighbourhood of the carbon band at  $3\cdot5\mu$ . An observation pointing to this possibility was made when investigating the effect of the air contained in the charcoal pores on the accuracy of the present adsorption measurements. This air is displaced during the experiment, and thus while the initial weight of charcoal is that of the charcoal plus the air in the pores, after the experiment the charcoal is weighed plus the adsorbate, but minus the expelled air. To determine the error thus introduced, charcoal was sealed up in glass bulbs which could be broken by a brass screw working through an air-tight sleeve in a brass cylinder which was connected to a water-jacketed gas burette. By these means, the bulb containing the charcoal could be broken in the cylinder under an excess of any given liquid, and the air expelled could be measured. Of sixteen liquids so examined fourteen displaced between 6·5 and 6·8 c.c.s of air (*N.T.P.*) per gram of charcoal in periods varying from 5 minutes to 20

<sup>5</sup> Baker, *J. Chem. Soc.*, 1927, 130, 949.

<sup>6</sup> Baly, *Rice Inst. Pamphlet*, 1925, 12, 1.

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hours. The error introduced into the adsorption measurements by this loss is slight and is balanced by the small loss of vapour which occurs after opening the tube at the end of the experiment. Carbon tetrachloride and tetrachlorethylene, however, after 20 hours had expelled less than 1.0 c.c. of air per gram of charcoal. The abnormal behaviour of these two substances cannot be explained by their rather large molecules blocking the pores of the charcoal, since ethylene dibromide, with a still larger molecular volume, displaced the maximum amount of air in a few minutes. Nor is any explanation possible in terms of the varying solubility of air in the liquids examined, for *n*-pentane, with an extremely low solubility for air, displaced the full quantity of air from the charcoal in a short time. Further, since this same reluctance to enter the charcoal is found for carbon tetrachloride in the vapour phase, the anomaly cannot be due to a low penetration coefficient for the liquid. It is, however, striking that of the numerous organic substances examined by Coblenz<sup>7</sup> in the infra-red region these two alone failed to show the characteristic carbon band at  $3\cdot5\mu$ . If the above tentative suggestion of the importance of the infra-red band of carbon in connection with the adsorptive power is considered, it is evident that carbon should have a negligible adsorptive power for carbon tetrachloride and tetrachlorethylene, since these substances could not take part in energy transfers occurring in the region of  $3\cdot5\mu$ .

*The Third Stage.*—In the majority of adsorption curves shown in Fig. 1, it will be seen that the third stage of adsorption is represented by straight lines, which are not parallel to those found for the first stage. If, however, lines are drawn representing the composition of the bulk equilibrium liquids in the various series, it will be found that they are, within extremely small limits parallel with those representing the third stage of adsorption. Thus the third stage consists in the isothermal distillation of the bulk liquid over to the charcoal. In one or two series in which this process was carefully followed for more than three weeks, it was found that the lines representing the third stage did not become strictly parallel to those representing the composition of the bulk liquid until 14 to 20 days had elapsed. These lines are therefore to be regarded as approaching asymptotically to lines parallel to those of the bulk liquid composition. For this reason, the third stage is considered to consist in the gradual filling up of the intergranular spaces of the charcoal, after the internal pores of the charcoal have been filled with adsorbate which has come into equilibrium with the vapour phase. This intergranular condensation will begin at the points of contact of the charcoal particles, and in its initial stages will give rise to surfaces having a marked concave curvature, and therefore vapour pressures somewhat different from that of the bulk liquid. As the spaces are gradually filled, the liquid condensing will gradually approach in composition that of the bulk liquid giving rise to adsorption curves of the type observed. The nature of the third stage renders possible the calculation of the composition of the adsorbate at the second break point in those cases in which coalescence of the second and third stages has occurred. In those series in which all three stages were sharply defined, it was shown that the replacement in the second stage occurred practically without change in the volume of the adsorbate, and that the mean value of this volume, for a gram of the charcoal used was 0.1575 c.c. Thus if we produce the lines representing the third stage backwards towards the origin, and calculate at what number of total mols. adsorbed, the sum of the volumes of the two components

<sup>7</sup> Coblenz, Carnegie Inst. Pubs., 35 (1905).

adsorbed, as represented by points on the above lines, is 0·1575 c.c., we shall have determined, *ipso facto*, the composition of the adsorbate at the second break point. This was done, as mentioned above, for the butyl alcohol-benzene series.

### Summary.

The adsorption by a coconut charcoal has been measured for the binary vapour systems methyl alcohol-benzene, ethyl alcohol-benzene, *n*-propyl alcohol-benzene, and *n*-butyl alcohol-benzene at 20°.

Adsorption occurs in three stages which represent respectively (*a*) the adsorption of a vapour phase, (*b*) the condensation of the vapour phase followed by a change in composition of the liquid so formed in an effort to reach equilibrium with the bulk equilibrium liquid, and (*c*) capillary condensation in the inter granular spaces of the charcoal.

The first stage is mainly diffusional in character, and selective adsorption is either absent or slight.

The selective action of the charcoal is exhibited chiefly in the second stage.

It is suggested that the selective adsorption is the result of the adsorbent altering the vapour pressures of the components of the adsorbate in different degrees, with the result that a liquid adsorbate may have the same vapour pressure as a bulk liquid of different composition.

A possible quantum mechanism involving energy transfers in the infra-red region is suggested for the above effect.

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## THE INTERACTION OF CHLORINE AND SULPHUR MONOCHLORIDE. PREPARATION OF SULPHUR DICHLORIDE: USE OF ANTIMONY PENTA-CHLORIDE AS CATALYST.

By RICHARD PARKINSON BOTHAMLEY.

(Communicated by PROFESSOR F. S. KIPPING.)

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It was observed by Aten<sup>1</sup> that chlorine and sulphur monochloride combine only very slowly at room temperature, the yellow liquid gradually changing to red. The process may be expedited by cooling the reaction vessel in ice; also by the addition of certain catalysts.

In 1918 Pope and Heycock<sup>2</sup> stated that by the addition to the sulphur monochloride of 1 per cent. by weight of "absorbent charcoal" the reaction may be accelerated, and that "this material is considerably superior to the catalysts hitherto proposed to be used for the purpose in view;" but they do not say how the charcoal was prepared, nor do they give any quantitative data as to the acceleration.

In the course of some experiments carried out by the author, antimony

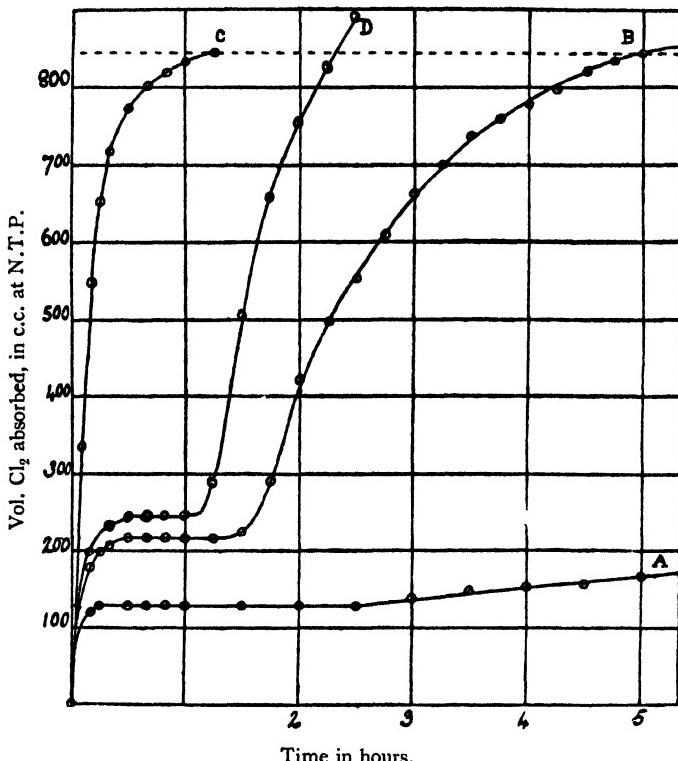
<sup>1</sup> Aten, *Z. physikal. Chem.*, 1906, 54, 72.

<sup>2</sup> Pope and Heycock, (B.P. No. 142879).

pentachloride was found to be a very efficient catalyst for the reaction  $S_2Cl_2 + Cl_2 = 2SCl_2$ , the addition of 0·5 per cent. by weight causing the absorption of the theoretical quantity of chlorine in about an hour at atmospheric temperature ( $19^\circ$ —curve C).

A larger proportion (1·2 per cent.) of the catalyst caused no further acceleration. In the absence of a catalyst (at  $16^\circ$ ) only about one-fifth of the theoretical quantity of chlorine had been absorbed in 5 hours (curve A); and even when the reaction vessel was cooled in ice 5 hours were required for completion of the reaction (curve B).

The dotted horizontal line in the figure indicates the theoretical quantity of chlorine required for the complete conversion into sulphur



A. Pure  $S_2Cl_2$  at  $16^\circ C.$  B. Pure  $S_2Cl_2$  at  $0^\circ C.$  C. 0·5 per cent.  $SbCl_5$  present, at  $19^\circ C.$  D. Pure  $S_2Cl_2$  at  $0^\circ C.$  in bright sunlight.

FIG. I.

dichloride ( $SCl_2$ ) of the amount of sulphur monochloride employed. All volumes are reduced to *N.T.P.*<sup>3</sup>

The antimony pentachloride dissolves readily in the sulphur monochloride, but on passing chlorine through the solution a colourless precipitate is formed, presumably the compound  $SbCl_5SCl_4$ , obtained by Ruff

<sup>3</sup> In experiments carried out at room temperature absorption of chlorine ceased when the liquid contained about 70 per cent. Cl ( $SCl_2 = 68\cdot9$  per cent. Cl). At  $0^\circ$ , however, absorption proceeded beyond this point.

The nature of the product  $SCl_2$  is not discussed (*cf.* Ruff and Fischer, *Ber.*, 1903, 36, 418; Aten, *Z. physikal. Chem.*, 1906, 54, 55; Bergmann and Bloch, *Ber.*, 1920, 53, 977; Lowry, McHatton, and Jones, *J. Chem. Soc.*, 1927, 746).

and Fischer<sup>4</sup> by adding  $\text{SCl}_2$  to a cold solution of antimony pentachloride in sulphuryl chloride.

The curves A and B for pure sulphur monochloride show that after the first 20 minutes or so there is a period of quiescence during which no absorption of chlorine occurs. At the beginning of this period the liquid is yellow, but towards the end it gradually becomes red; absorption is then renewed, and proceeds continuously. These observations agree with those of Aten,<sup>1</sup> the initial absorption being presumably a physical solution of chlorine in sulphur monochloride.

The occurrence of a period of induction suggested that the reaction might be a photochemical one, as are many reactions of chlorine, e.g., chlorine and hydrogen;<sup>5</sup> and as all the experiments described above were carried out in dull diffused daylight, the effect of exposure to direct sunlight was examined, the reaction vessel being cooled in ice as in B. A comparison of the results (curve D) with those obtained at 0° in dull diffused daylight (curve B) shows that the period of induction is shorter, and the absorption, when renewed, proceeds more rapidly, than is the case in dull diffused daylight; the time required for completion of the reaction in the former case is less than half of that required in the latter.

## Experimental.

Fig. 2 shows the apparatus employed. Chlorine, washed with water (B), and dried with sulphuric acid (C and D), was passed into the graduated cylinder G, which was filled with concentrated sulphuric acid saturated with chlorine,<sup>6</sup> until most of the acid had been driven over into K. The taps L and P were then opened, and the current of gas continued through M and N until all air had been expelled, when F and P were closed. By raising or lowering K the gas in G and N was brought under atmospheric pressure, and the level of acid in G was noted.

A measured quantity (3 c.c.) of pure sulphur monochloride,<sup>7</sup> or of the sulphur monochloride containing a known weight of antimony pentachloride, was then introduced into O, and by momentarily opening P, was allowed to

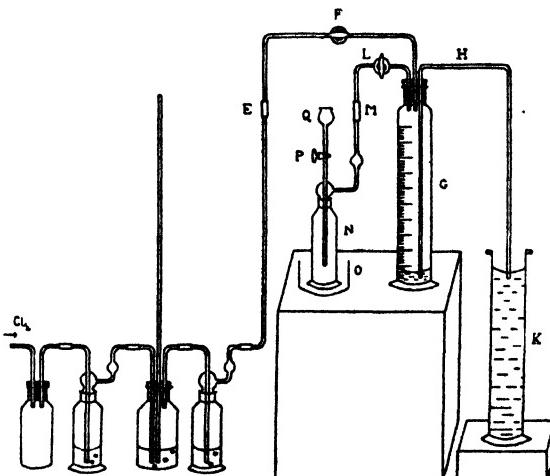


FIG. 3.

<sup>4</sup> Ruff and Fischer, *Ber.*, 1994, **37**, 4515.

<sup>5</sup> Cf. Bunsen and Roscoe, *Phil. Trans.*, 1857, 147, 381; Burgess and Chapman, *J. Chem. Soc.*, 1906, 89, 1390; Norrish, J., *ibid.*, 1925, 127, 2323.

<sup>6</sup> In order to fill G with acid the tube F was disconnected at E from the chlorine supply and connected to a water-pump, by means of which the acid was drawn in through H from K, which was raised on a level with G.

<sup>7</sup> Cf. Mann, Pope and Vernon, *J. Chem. Soc.*, 1921, 119, 636.

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run into N, which was surrounded by a glass basin O, for containing ice when necessary. N was gently agitated from time to time. As absorption proceeded, K was slowly raised so as to keep the gas under atmospheric pressure during the whole experiment.

Before beginning the series of quantitative experiments the cylinder G was filled with chlorine and allowed to stand for about a week, the chlorine being renewed every day, in order to "season" the rubber cork.

### Summary.

The effect of the addition of antimony pentachloride on the rate of chlorination of sulphur monochloride has been measured.

Evidence is furnished that the reaction between chlorine and sulphur monochloride is a photochemical reaction.

The author wishes to express his thanks to the Council of the University College, Nottingham, for affording him facilities for carrying out this research; and to Professor F. S. Kipping, F.R.S., for his kindly interest and supervision during the course of the work.

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## NOTE ON THE INFLUENCE OF HYDROLYSED GELATIN ON THE PRECIPITATION OF SILVER CHROMATE.

By T. R. BOLAM AND B. N. DESAI.

*Received 4th November, 1927.*

It has been shown<sup>1, 2</sup> that gelatine has to a marked degree the power of retarding the separation of silver chromate from aqueous mixtures of silver nitrate and potassium chromate. With sufficient gelatin the mixture will remain clear and yellow for 72 hours, although the solution is strongly supersaturated with silver chromate.

No experiments seem to have been carried out to determine quantitatively how the inhibitive influence is affected by hydrolysis of the gelatin. It may be mentioned that Liesegang<sup>4</sup> states that the solubility of silver chromate in "gelatose" alone is less than in mixtures of "gelatose" with gelatin.

The gelatin was hydrolysed by heating a solution (3 per cent. or 6 per cent.) on the water-bath or by gentle boiling. For these operations it was placed in a fused silica flask fitted with a water-cooled ground-in fused silica condenser. The flask and its contents were weighed before and after each period of heating and any loss in weight, always small, made good by the addition of water.

In all experiments, 5 c.c.  $N/100 K_2CrO_4$  + 3·8 c.c. 3 per cent. gelatin was added to 5 c.c.  $N/100 AgNO_3$  + 3·8 c.c. 3 per cent. gelatin. Gelatin B<sup>2</sup> and pure salts were used and all solutions were made up with con-

<sup>1</sup> Williams and MacKenzie, *J.C.S.*, 117 (1920), 844.

<sup>2</sup> Bolam and MacKenzie, *Trans. Far. Soc.*, 221 (1926), 151, 162.

ductivity water. The reacting solutions were prepared in pyrex test-tubes, brought to approximately  $25^{\circ}$  C., mixed by pouring from tube to tube several times, and then immediately placed in a  $25^{\circ}$  C. thermostat. The time required for the appearance of a definite red colour was taken as the measure of the inhibition.

The  $\rho_H$  of the gelatin at the various stages of hydrolysis was determined colorimetrically, using brom-cresol-purple as indicator and Sorenson's phosphate mixtures as standards. The gelatin was considerably diluted for this purpose.<sup>2</sup>

The following are the figures for three entirely independent series of experiments :—

Treatment.	(t) Time for appearance of precipitate (mins.).			$\rho_H$ .
	1.	2.	3.	
3 per cent. gelatin heated on water-bath for :—				
1 hour . . . . .	43	41	39	5'9
2 hours . . . . .	44	42	42	5'9
2 hours + 1 hour boiling	70	57	62	5'9-5'95
" " + 2 hours "	47	52	56	5'95
" " + 3 " "	57	50	42	5'95
" " + 5 " "	59	52	—	5'95
" " + 7 " "	41	—	—	5'95-6'0

For comparison "*t*" was determined for the unhydrolysed gelatin (dispersed at  $30^{\circ}$  to  $35^{\circ}$  C.) and found to have the following values in four independent experiments: 146, 130, 134, 161 mins. The  $\rho_H$  of the unhydrolysed material proved to be 5'75 and the question arises whether the marked loss in effect on hydrolysis is not due simply to decrease in acidity.<sup>2</sup> To test this, 6 per cent. gelatin was heated on the water-bath for one hour and then diluted to 3 per cent. with acetic acid of such strength that the  $\rho_H$  of the gelatin was brought back to approximately its original value. Also 3 per cent. unhydrolysed gelatin was prepared containing the same amount of acetic acid. Whereas in the case of the latter "*t*" underwent a large increase (*t* = 220 and 251 mins.: indep. expts.), the inhibitive capacity of the hydrolysed gelatin was not affected (*t* = 38 and 35 mins.: indep. expts.).

It was found that the hydrolysis of the gelatin produced considerable changes in the formation and appearance of the precipitate, which may be broadly summarised as follows :—

#### Unhydrolysed gelatin.

1. Precipitation localised at certain points.
2. Mixture becomes turbid red.
3. Precipitate settles much more rapidly than in the case of hydrolysed gelatin.

#### Hydrolysed gelatin.

- Precipitate appears uniformly in all parts.
- Mixture becomes clear red.

The hydrolysis thus increases the degree of dispersion of the precipitate, which is in agreement with the work of Ganguly<sup>3</sup> and is, as pointed out by him, due to a stronger "protective" action.

While the data given above are rather approximate, owing, probably, to the simple method of mixing and to inadequate control of temperature

<sup>2</sup> Ganguly, Quart. J. Indian Chem. Soc., 3 (1926), 177.

during hydrolysis, there is clear indication of a maximum in the value of "t" at a certain stage.

Liesegang<sup>4</sup> found that for the formation of periodic structures of silver chromate in gelatin a certain proportion of the hydrolysis products of the latter is necessary. In view of the weak inhibitive power of "gelatose" this is surprising, and suggests that the inhibitive influence of a mixture of gelatin and gelatose is greater than might be expected from the behaviour of its constituents.

From the foregoing it will be seen that the decrease in inhibitive capacity on hydrolysis is due to the fundamental changes produced in the gelatin. Further, it is obvious that inhibition and protection *do not go hand in hand*. It must be remembered that there is a difference in function. In the case of the first the gelatin operates by opposing the formation or growth of crystallisation centres or nuclei. Svedberg's<sup>5</sup> work on the reduction of gold chloride in the presence of gelatin, and that of Marc<sup>6</sup> on the crystallisation of  $K_2SO_4$  in the presence of certain dyestuffs, provide examples of similar action. On the other hand "protection" prevents the aggregation of small particles to larger masses.

<sup>4</sup> Liesegang, *Koll. Z.*, **2** (1907), 70; *Z. physik. Chem.*, **88** (1914), 1.

<sup>5</sup> Svedberg, *Koll. Z.*, **5** (1909), 318.

<sup>6</sup> Marc, *Z. physik. Chem.*, **67** (1909), 470.

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## REVIEWS OF BOOKS.

**Molecular Physics and the Electrical Theory of Matter.** By J. A. CROWTHER, M.A., Sc.D., F.Inst.P. (London: J. & A. Churchill. Pp. viii + 202. Price 7s. 6d.) Fourth Edition.

To meet the views of the hypercritical the fourth edition is given a sub-title. This little book, however, is so well known by its earlier editions that it is unnecessary to detail its contents. The main alterations are in the expansion of the later portions of the book at the expense of the description of the earlier theories.

**The Higher Coal-tar Hydrocarbons.** By A. E. EVEREST, D.Sc., F.I.C. (London: Longmans, Green & Co., Ltd. Pp. xiii + 334. Price 18s. net.)

No excuse is needed for noticing a book on Organic Chemistry in these columns if it is so useful a compilation as that of Dr. Everest. There have been brought into small compass the known facts about the coal-tar hydrocarbons of greater complexity than naphthalene and anthracene; for convenience the author classifies them in four groups, Acenaphthene, Fluorene, Phenanthrene, and miscellaneous. In a final paragraph the author draws attention to the very complex condensed nuclei that have resulted from syntheses carried out in connection with dyestuffs research and suggests that interesting results might arise by applying X-ray methods.

## *GENERAL DISCUSSION*

ON

# **COHESION AND RELATED PROBLEMS**

HELD BY THE FARADAY SOCIETY ON 23RD NOVEMBER, 1927.

## **COHESION: A GENERAL SURVEY.**

INTRODUCTORY PAPER BY THE PRESIDENT (PROFESSOR C. H. DESCH,  
D.Sc. F.R.S.).

*Received 12th November, 1927.*

In a valuable review of the subject of internal pressures by Professor T. W. Richards of Harvard,<sup>1</sup> attention is called to a passage in the third edition of Newton's "Opticks"<sup>2</sup> which runs as follows:—

"The Parts of all homogeneous hard Bodies which fully touch one another, stick together very strongly. . . . I . . . infer from their Cohesion, that their Particles attract one another by some force, which in immediate Contact is exceeding strong, at small distances performs the chymical Operations above mention'd, and reaches not far from the Particles with any sensible Effect. . . . There are therefore Agents in Nature able to make the Particles of Bodies stick together by very strong Attractions. And it is the Business of experimental Philosophy to find them out."

This passage admirably states the problem of cohesion. Whilst much attention was given to the problem by the successors of Newton, and by the physicists of the earlier part of the nineteenth century, it was passed over lightly in most text-books of the latter part of that century, and it is only recently that it has again assumed prominence. The holding of a *General Discussion* at the present moment seems to be justified by the interest in the subject which is now being taken by engineers and metallurgists as well as by students of physics. This interest has been aroused by certain difficulties which present themselves in the course of the study of the strength of materials under various conditions of service. The engineer formerly obtained sufficient information as to the strength of most of his materials by tests of a comparatively simple kind. For example, in the universally adopted tensile test, a specimen of standard shape is pulled in the direction of its axis, and the load per unit area needed to break it is determined, whilst the permanent elongation produced before fracture is also measured. The first is an indication of the tenacity, the latter of the ductility of the specimen, but neither is a definite physical constant of the material. Brittleness is measured by determining the energy absorbed when a notched bar is broken by impact. In modern machinery working at very high speeds, and especially in aeroplane engines and similar machines, the essential properties of the materials are not fully revealed by the tensile test, and various forms of fatigue test have been devised and are currently employed. Again, whilst most metals and other structural materials are made up of a very large number of minute crystals with random orientation, so that for practical purposes they may be treated as if they were isotropic, metallurgists have recently become interested in the behaviour of large single crystals of metals,

<sup>1</sup> *Chemical Reviews*, 1925, 2, No. 3.

<sup>2</sup> Sir I. Newton, "Opticks," 3rd ed., 1721, p. 363.

which have very different properties, some of which will find practical application. There is reason to believe, also, that fatigue is intimately connected with the internal crystalline structure, and that for its study it is not sufficient to regard the material as isotropic. The method of X-ray examination has made it possible to connect the problem of deformation with that of structure.

The phenomena of interest to the engineer and metallurgist, depending on the nature of cohesion, may be summed up as follows:—

1. The tenacity of metals, of crystals such as rock salt, and also of glassy substances, as determined by a tensile test, is very much less than that calculated from physical theory.
2. The so-called elastic limit is not a physical constant. The more delicate the extensometer used the lower is the stress at which permanent deformation is seen to begin. Single crystals appear to yield at the lowest stress which can be applied in a testing machine.
3. Failure by fatigue, that is, by repeated applications of stress, occurs under much lower ranges of stress than that required to produce failure under static loading.
4. The process of cold-working, or of deforming a solid at a temperature below some limiting temperature (usually about one-third of the absolute temperature of melting) alters the properties of the material to a remarkable extent.
5. The manner of deformation depends to a great extent on the rate of application of the stress, and the time during which it is applied.
6. In bodies composed of many crystals, there is a marked difference between the properties of the interior of crystals and their boundaries which is imperfectly understood, and this difference is of importance in relation to many facts of strength and fatigue.
7. The nature of crystal surfaces is of importance in the study of lubrication, where solid surfaces are separated by a thin liquid film, and in that of welding and sintering, in which surfaces are united by contact at temperatures below the melting-point. Closely connected with this is
8. The problem of adhesives and solders, or materials, thin films of which can firmly unite solid masses, and that of the adhesion of coatings of foreign material deposited by electrolysis or other processes.
9. Diffusion can occur in solids, and is of importance in many technical processes. It is not certain whether it takes place by change of place of atoms in an undisturbed lattice, or whether previous loosening of the lattice is essential.

These points may be briefly discussed.

1. Under hydrostatic compression solids are perfectly elastic, allotropic change being excluded. Hooke's law is not obeyed, as the compressibility diminishes with increasing pressure. The real tenacity of a solid should be determined by measuring its strength in uniform tension, but there is no easy method of making the experiment. When simple tensile stress is applied to a ductile material the specimen fails by shearing, one part slipping over another, and the more ductile the metal the more shearing occurs before rupture. So-called "triple-tensile stress," by which a body is subjected to outward tension in all directions, is very difficult to obtain. It has been approximately reached by Joffé in an ingenious series of experiments with rock salt,<sup>3</sup> spheres of the mineral being cooled very

<sup>3</sup> Joffé and Lewitsky, *Z. Physik.*, 1926, 35, 442.

carefully in liquid air and then immersed in a bath of molten lead. The maximum tension can be calculated from the difference between the temperature of the bath and that of the mass. In this way tensile strengths far greater than that found by ordinary methods have been obtained, rock salt giving a strength in excess of  $70 \text{ kg./mm.}^2$  instead of  $0.45 \text{ kg./mm.}^2$ . The strength calculated on the basis of electrical theory is about  $200 \text{ kg./mm.}^2$ .

This kind of stress has also been called "clink stress," and is of great importance in the manufacture of steel, but its quantitative study presents difficulties. When an ingot cools in its mould, or when an ingot or forging is heated in a furnace, the difference of temperature between the outer layers and the interior may set up stresses exceeding the tensile strength of the steel, so that internal cracks or "clinks" are produced. As such masses are not spherical, the distribution of the stress is complex, and pure "triple-tensile" stress is not realised. A mathematical analysis should, however, show that rupture under such conditions occurs at a higher stress than when the same steel is broken in a tensile test.

The "maximum stress" recorded in the tensile test of the engineer does not at all represent the true breaking stress of a ductile material, because the cross-sectional area of the specimen is diminishing during the test, whilst the load is calculated with reference to the original area. When the true stress is plotted against the reduction of area of section a curve is obtained which is a truer representation of the relation between stress and strain. From the point at which plastic yielding begins this curve, for many metals, approaches very closely to a straight line. This part of the subject is dealt with in the papers by Professor Polanyi and Dr. Sachs.

A brittle substance breaks in tension without appreciable extension or reduction of area, showing that slip does not occur. In this instance also, the observed tensile strength is far below that calculated for crystals from electrical theory, or for glass from measurements of surface tension. In part this is due to accidental causes, as is shown by rock salt, a substance which under ordinary conditions breaks without appreciable deformation when bent or submitted to tensile stress. It was shown by Coblenz in 1903, however, that slips of the mineral could be bent in water, and this observation, brought to the notice of physicists at the British Association meeting in Edinburgh in 1921 by Professor R. W. Wood, has since attracted much attention. Under such conditions the crystal is plastic and undergoes considerable deformation before breaking. It has been suggested that the premature rupture is due to the presence of minute sharp cracks on the surface, causing an intense localisation of stress, and that the effect of the water is to dissolve the surface and, thus, to round off or entirely remove the crack. Tensile strengths as high as  $160 \text{ kg./mm.}^2$  were observed.<sup>4</sup>

In accordance with this view, rock salt does not become plastic when oil or saturated brine is used in place of water.

The difference between the calculated and observed strengths of brittle substances was explained by Griffith<sup>5</sup> as being due to the presence in ordinary substances of large numbers of minute cracks, causing local internal intensifications of stress, and this view has received Continental support, a mathematical analysis of the conditions having been undertaken by Wolf<sup>6</sup> and others. Experimental evidence for the explanation was

<sup>4</sup> Joffé and Lewitsky, *Z. Physik*, 1925, 31, 576.

<sup>5</sup> Griffith, *Phil. Trans.*, 1920, 221 A., 163.

<sup>6</sup> Wolf, *Z. angew. Math.*, 1923, 3, 107.

brought forward by Griffith, who was able to prepare fibres and even rods of glass and vitreous silica, by heating to a very high temperature and then drawing slowly, which had an enormously increased elasticity and tensile strength, but which were in an unstable condition, reverting to the usual weak state on being scratched, and diminishing in strength with time. Glass which normally broke under a tensile stress of  $17.5 \text{ kg./mm.}^2$  when drawn in this way, gave tensile strengths as high as  $222 \text{ kg./mm.}^2$ , the strength increasing with diminishing diameter of the fibre, and extrapolation to zero diameter gave a limiting value (corresponding with molecular dimensions) of  $715 \text{ kg./mm.}^2$ . The silica rods could be bent to a very small radius, and when fracture occurred it was of an explosive character, even the thick ends attached to the fibre being shattered by the stresses set up by an elastic wave. It has not yet been found possible to obtain metals in a similarly strong condition.

**2.** Permanent deformation may be detected at lower loads than the elastic limit as measured by an extensometer, by using a heterodyne arrangement similar in principle to Whiddington's ultramicrometer.<sup>7</sup> Specimens of nickel were observed to yield under low stress and then to become elastic again until a higher stress was reached at which further yield occurred. Copper yields slightly even at the lowest stresses which are measurable in an ordinary testing machine. Single crystals, such as those of aluminium, yield plastically under very small stresses and do not obey Hooke's law when tested in the laboratory, using delicate extensometers.<sup>8</sup> Single crystals of rock salt, on the other hand, when examined by means of X-rays, show a definite and well-marked stress at which distortion of the pattern begins. Below that limit, there is no distortion of the X-ray pattern, even in six hours, whilst under a slightly higher stress distortion is visible in a few seconds. The elastic limit thus defined becomes lower with rising temperature, becoming zero at the melting-point.<sup>9</sup>

Deformation of a single crystal takes place by slipping along certain closely packed planes of atoms. The simplest case is that of zinc, in which slipping is for the most part confined to the basal plane.<sup>10</sup> Such crystals have been found to have a definite elastic limit under shear of about  $0.036 \text{ kg./mm.}^2$ , increasing at the temperature of liquid air to  $0.126 \text{ kg./mm.}^2$ , and definite values are also found for the other planes of possible slip.<sup>11</sup> Single crystals of aluminium are usually recorded as having no elastic limit, and as yielding plastically under the smallest load, but it does not appear that measurements under such very small loads have been made with this object, and it appears inconceivable that there is no limit below which yielding does not occur.

The raising of the elastic limit by deformation is considered under (4).

**3.** The relations between cohesion and fatigue are dealt with in the papers by Mr. Gough and Professor Haigh. A stress which is far below that needed to cause fracture under static conditions will break a material if repeated a sufficient number of times. The higher the stress, the smaller the number of repetitions which the material can withstand. The range of stress varies, according as the mean stress is zero, that is, the repeated

<sup>7</sup> Handford, *Phil. Mag.*, 1924, **47**, 807.

<sup>8</sup> Gough, Hanson, and Wright, *Phil. Trans.*, 1926, **226 A.**, 1.

<sup>9</sup> Joffé, Kirpitschewa, and Lewitsky, *Z. Physik.*, 1923, **22**, 286.

<sup>10</sup> Mark, Polanyi, and Schmid, *ibid.*, 1922, **12**, 78.

<sup>11</sup> Schmid, *Intern. Congr. Angew. Math.*, 1924.

stresses are alternately equally positive and negative, or as there is a finite mean stress. There is a very large amount of published work on this subject, to which it is not necessary to refer in this place. The important fact is that failure by fatigue may occur either with or without permanent deformation, but with an increase in the hardness of the stressed portion. It is usually assumed that there is a definite range of stress below which failure will not occur, however many times it is applied, and although this conclusion is by its nature incapable of direct proof, the evidence is in its favour. This "fatigue limit" is obtained by extrapolation of the curve connecting range of stress with endurance, which becomes asymptotic to the value of stress corresponding with it. Single crystals as well as aggregates exhibit such a fatigue limit, and lend themselves well to its study. Since, however, slip occurs very readily in single crystals, some extension always takes place in them under alternating stress.<sup>8</sup>

Whilst slip occurs in the early stages of a fatigue test of a metal composed of small crystals, and may be recognised under the microscope, the effect is often merely a redistribution of stress between different crystals, and there is no change in the microscopical structure which can be correlated with the reaching of the fatigue limit.<sup>12</sup>

4. Slip in a crystal increases the resistance to further slip; the substance is hardened or strengthened by plastic deformation. There are many rival theories of this hardening, which it is not necessary to discuss in detail. Plastic deformation at a temperature below the temperature of recrystallisation, which is for most metals in the neighbourhood of one-third of the melting-point, reckoned on the absolute scale, raises the elastic limit for stresses of the same kind, and also the breaking load in the ordinary tensile test, but does not, so far as the available evidence goes, increase the actual stress under which the material finally breaks. This is shown by Fig. 1, plotted from results obtained for copper by W. Muller (1918).<sup>13</sup>

The true stress-strain curves for copper in different degrees of cold-working converge to a value at about 66 kg./mm.<sup>2</sup>, which represents the tensile strength which would be obtained if it were possible to draw the test-piece out to a point, so that the cross-sectional area at fracture would be zero.

The physical properties of a metal are profoundly changed by cold working. A soft metal, such as copper, may be made highly elastic, so that it will serve for springs, whilst at the same time the ductility is reduced. The density of a cold-worked metal is less than that of the same metal in the soft condition, and the electrical resistance is somewhat increased. It was these facts which led Beilby to suggest that the space lattice is partly broken down and replaced by a "vitreous" phase, usually spoken of as the "amorphous modification."<sup>14</sup> This hypothesis has been used with great success to explain the phenomena of deformation, but it is not universally accepted. Other explanations depend on distortion of the space lattice to a degree short of destruction, or on a fragmentation of crystals, replacing a crystal of larger size by an aggregate of smaller units of diverse orientation.<sup>15</sup> Examination by means of X-rays makes it possible to follow distortion of

<sup>12</sup> Gough and Hanson, *Proc. Roy. Soc.*, 1923, 104 A., 538.

<sup>13</sup> Quoted from Sachs, *Mechanische Technologie der Metalle*, Leipzig, 1925.

<sup>14</sup> See Beilby, *Aggregation and Flow of Solids*, London, 1921, for discussion and references.

<sup>15</sup> See, for the discussion of these hypotheses, Sachs, *op. cit.*; Jeffries and Archer, *The Science of Metals*, New York, 1924; Rosenhain, *Physical Metallurgy*, London, and papers contributed to the present meeting.

the space lattice, but there are also advantages in making experiments with transparent substances, such as rock salt and ammonium nitrate, which can be obtained in large single crystals, and may be examined in polarised light.

5. The influence of the rate of application of stress on the deformation produced by that stress deserves more attention than it has received hitherto. Elastic deformations are transmitted through a solid with the velocity of sound, but it is probable that a certain minimum time of application is necessary before plastic flow can be produced. It was found by Hopkinson<sup>16</sup> that a copper wire might be stretched by a tensile stress beyond its elastic limit and even beyond its static breaking stress, and yet remain perfectly elastic, provided that the time of application of the stress did not exceed 0·001 second. Similarly, in Jenkin's experiments on transverse alternating stress<sup>17</sup> it was found that when the frequency of alternation was increased, the stress necessary to cause fracture by fatigue rose, and

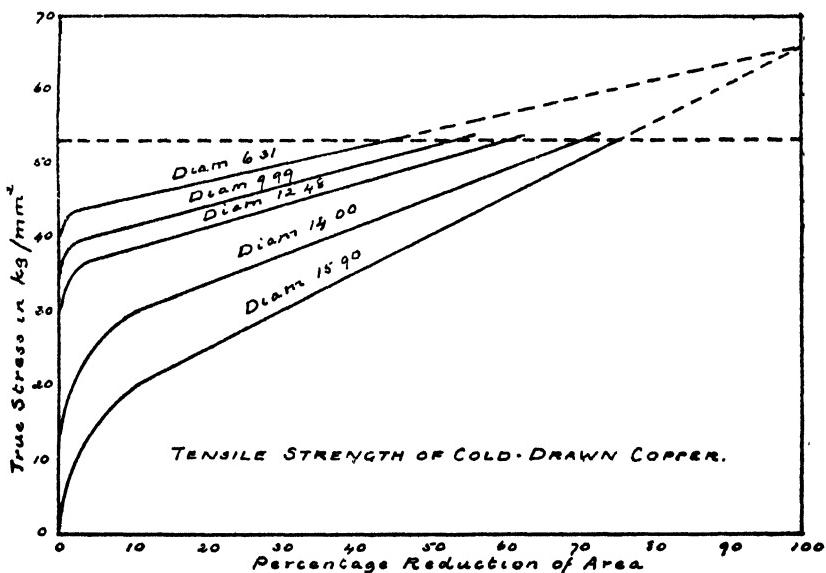


FIG. I.

there was some indication that at sufficiently high frequencies it would be impossible to produce the effects of fatigue.

A twisted wire does not return to its original condition immediately the stress is removed, even when that stress was within the elastic range, but a certain time elapses, during which a slow return is taking place. This was discovered by Weber,<sup>18</sup> and is known as elastic after-working. It has been stated not to occur in single crystals of tungsten, and has therefore been associated with the boundaries between the crystals in an ordinary specimen of metal. The behaviour of other single crystals in this respect calls for more complete investigation. It is shown in Mr. Gough's paper in the present discussion that elastic hysteresis is found in single crystals as well as in aggregates, and this property probably bears some relation to after-working.

<sup>16</sup> Hopkinson, *Proc. Roy. Soc.*, 1905, **74 A.**, Collected Papers, 1920, 49.

<sup>17</sup> Jenkin, *Proc. Roy. Soc.*, 1925, **109 A.**, 119.

<sup>18</sup> Weber, *Pogg. Ann.*, 1835, **34**, 247; 1841, **54**, 9.

At temperatures not too far removed from their melting-points, metals and no doubt other crystalline substances undergo viscous flow to a greater or less extent, that is, deformation continues under constant stress. This fact has become of great importance in engineering industry, on account of the combination of high stress and high temperature which materials are called on to withstand in high-pressure steam boilers, oil-cracking vessels, synthetic ammonia vessels, and similar plant. As the temperature falls the viscous flow diminishes, and it becomes inappreciable at the ordinary temperature for steel and other metals of high melting-point, whilst lead and tin have to be cooled in liquid air to cause the effect to vanish entirely.<sup>19</sup> At high temperatures the effect may become very large, and it has been the subject of many recent investigations, beginning with that of Dickenson on a series of steels and a nickel-chromium alloy.<sup>20</sup> For details, reference may be made to the principal memoirs.<sup>21</sup>

In the tensile experiments made by Andrade, the elongation under stress could always be represented by the simple formula,

$$l = l_0(1 + \beta t^{\frac{1}{3}})e^{kt},$$

$l$  being the length and  $t$  the time, the exponential term representing the viscous part of the deformation. In the materials studied by other workers, it has not been found possible to express this part of the flow by a simple exponential term, and the variation of deformation with time is complex. Michelson<sup>22</sup> has divided the observed strains in his torsional experiments into the following parts: Elastic displacement, following Hooke's law and independent of time; elasto-viscous displacement, involving slow return after removal of stress; viscous displacement, exponential in character and not involving return; lost motion, or deformation occurring in very short time and not involving return. Michelson's treatment has not to my knowledge been applied to other experimental results, but it is evident that an exact study of viscous flow and its relation to plastic flow is of great importance for the explanation of the phenomena of deformation and their relation to cohesion.

Viscous flow is not a property of crystal aggregates only, but has been observed also in single crystals of tungsten. The actual amount of flow varies with the orientation, but the velocity of flow,  $\frac{dl}{dt}$ , varies exponentially

with the load  $R \frac{dl}{dt} = \frac{C}{R} e^{BR}$ ,  $B$  and  $C$  being constants.<sup>23</sup>

6. Ordinary metals are composed of many crystals of varying orientation, their boundaries being of irregular form. Under normal conditions, these boundaries behave as if they were stronger than the crystals themselves, so that fracture occurs through the crystals rather than between them, but at high temperatures this is often reversed, and the fracture passes by preference between the crystals. Such intercrystalline fractures are also characteristic of certain states of brittleness due to internal stress or to the action of gases,

<sup>19</sup> Andrade, *Proc. Roy. Soc.*, 1914, **90 A.**, 329. The fact had been established by Trouton and his collaborators.

<sup>20</sup> Dickenson, *J. Iron and Steel Inst.*, 1922, ii, 103.

<sup>21</sup> Lea, *Proc. Inst. Mech. Eng.*, 1924, 1053; Bailey, *J. Inst. Metals*, 1926, **35**, 27; Tapsell and Bradley, *ibid.*, 75; Sadler and Gregg, *Trans. Amer. Inst. Min. Met. Eng.*, 1927.

<sup>22</sup> Michelson, *Proc. Nat. Acad. Sci.*, 1917, **3**, 319.

<sup>23</sup> H. Schönborn, *Z. Physik.*, 1922, **8**, 377.

which penetrate more easily along the crystal boundaries than through their substance. It was suggested by Brillouin<sup>24</sup> and afterwards by Bengough<sup>25</sup> that the crystals are united by a film of amorphous material, the intercrystalline cement, which has the properties of an undercooled liquid, and is identical with the vitreous phase of Beilby. The development of this view is mainly due to Rosenhain, in whose hands it has been used most ingeniously to explain many of the peculiarities of the mechanical and chemical properties of metals and other crystalline solids.<sup>26</sup> It is assumed that when the growing surfaces of two crystals approach one another, as in the solidification of a mass of cast metal, a layer is left the atoms of which do not attach themselves to the space lattice of either, but remain in an unoriented condition which is comparable with that of an undercooled liquid. Granting the hypothesis, many consequences follow which can be verified by experiment. The initial difficulties in the way of its acceptance are, however, great, in connection with the question of the range of molecular forces, discussed at the close of this Introduction. The phenomena which have to be explained seem to call for an intercrystalline layer of considerable thickness, which would imply that the attraction of the neighbouring space lattices was sensible over a range of many, probably of many hundred, molecular diameters. No alternative hypothesis has, however, been worked out in detail, although Mr. Gough's paper contains an interesting suggestion. It may be expected that, as mentioned in the next section, the condition of one or two layers of atoms at the surface of a crystal will differ from that of the interior of the space lattice, and that an interfacial tension will exist between the face of a growing crystal and the liquid with which it is in contact during the process of solidification. The writer has given experimental evidence for the existence of such an interfacial tension in metals,<sup>27</sup> and this condition may be supposed to persist when the process is complete and the solid grains are in contact. Such a condition of tension, although only extending through a layer a few atoms thick, may explain some of the phenomena, but little has yet been done in this direction, failing satisfactory determinations of the magnitude of the surface tension effects.

7. That the surface of a crystal must differ in some degree in closeness of packing, and therefore in density, from the interior seems to follow from the unsymmetrical character of the cohesive forces in the layers of atoms nearest to the surface, which are attracted from below, but not from above. It has therefore been assumed that every crystal has a surface layer of lower density than the normal, this assumption having been previously made for liquids.<sup>28</sup> The consequences have been discussed by Edser.<sup>29</sup> Moreover, since there is no essential difference between cohesive forces and those of chemical affinity, the surface of a solid must possess residual affinity, which in a crystal will differ for different faces, being greater for planes of relatively open spacing than for those which are most closely packed. As it is in virtue of such forces that a crystal grows when placed in contact with a supersaturated liquid or vapour, closely packed planes are those of slowest growth, and also have least power of adsorbing foreign atoms, molecules or

<sup>24</sup> Brillouin, *Ann. Chim. Phys.*, 1898 (vii.), 13, 377.

<sup>25</sup> Bengough, *J. Inst. Metals*, 1912, 7, 123.

<sup>26</sup> Rosenhain and Ewen, *J. Inst. Metals*, 1912, 8, 149; Rosenhain, *Engineering*, 1913, 96, 537; *J. Inst. Metals*, 1923, 30, 3.

<sup>27</sup> Desch, *J. Inst. Metals*, 1914, II, 57; 1919, 22, 241; F. C. Thompson, *J. Iron Steel Inst.*, 1916, I, 155.

<sup>28</sup> Van der Waals, *Z. Physikal Chem.*, 1894, 13, 657.

<sup>29</sup> Edser, *Fourth Report on Colloid Chemistry*, London, 1922, p. 40.

ions. The evidence on these points has been reviewed by the writer elsewhere.<sup>30</sup>

Thin films of lubricant in contact with solid surfaces have their molecules in definite orientation with respect to that surface, as is shown by the very numerous investigations of I. Langmuir, Sir W. Hardy, and N. K. Adam. When a layer of lubricant separates two plane solid faces, the limiting condition is reached when the layer consists of two oriented layers one molecule thick, the plane of slip lying between them.<sup>31</sup> On the other hand, a film of this thickness has a quasi-solid character, and may offer a considerable resistance to shear, as in the "wringing" of two plane gauges together by means of a thin film of oil.<sup>32</sup>

Attempts have often been made to determine the force with which two plane surfaces of the same material will adhere when brought into close contact. Quantitative measurements of the kind have usually proved to be impracticable for two reasons. It is exceedingly difficult to prepare surfaces which are sufficiently plane to give contact over an appreciable area. Even with surface gauges, which are of extraordinary accuracy, the results of Holt and Barrell show that contact only occurs over a portion of the area, and that after many wrappings there is still a removal of metal from the spots in highest relief, this wear only disappearing gradually. "Seizing" of metallic surfaces is probably confined to a few spots only on each surface. Further, films of gas condense on the metal and alter its properties, so that the surface under examination is not that of the solid, but a layer of molecules of gas or other foreign matter attached to it. However, Hardy has found that glass may be prepared in such a state of cleanliness that a spherical surface cannot be drawn across a plane surface of the same material without tearing taking place, and many phenomena of the same kind are known. It seems natural to suppose that if two similar plane faces could be brought into actual contact, the attraction between them would be equal to the cohesion of that substance, and that perfect union would occur, but this condition is not easily realised. The welding of steel at temperatures at which the metal is plastic is an application of this fact. A flux is used to remove films of oxide, and the liquid slag so formed is expelled by pressure either by hammering or in the making of an electric resistance weld by squeezing. A properly made weld does not differ in strength or in structure from the original metal. (Arc-welding and oxy-acetylene welding, in which some of the metal is actually fused, belong to a different category.) The sintering of metallic powders is a similar process. Tungsten, the melting-point of which is too high to permit of fusion in manufacture, is compressed and strongly heated. In the subsequent swaging process the particles become united to a compact mass, and ultimately recrystallised. Union occurs at a temperature which is lower, the greater the precautions taken to avoid films of oxide or other impurity.<sup>33</sup>

8. For practical purposes it is convenient to distinguish cohesion between atoms, molecules, or ions within a mass of solid or liquid, from adhesion of one solid to another, or of a liquid to a solid, but there is no theoretical distinction of any importance between the two. It is most probable that the same forces are involved in both cases, and that differences are only due to differences in the relative intensity of those forces.

<sup>30</sup> Brit. Ass. Rep., 1925, 30; Trans. Amer. Inst. Min. Met. Eng., 1927.

<sup>31</sup> Hardy and Bircumshaw, Bakerian Lecture, Proc. Roy. Soc., 1925, 108 A., 1.

<sup>32</sup> Holt and Barrell, Proc. Roy. Soc., 1927, 116 A., 401.

<sup>33</sup> C. J. Smithells, Pitkin, and Avery, J. Inst. Metals, 1927, 38.

The adhesion between a solid and a liquid depends on the nature of both substances.<sup>34</sup> The union of two solid masses by interposing a film of some substance which at first is usually liquid but later becomes solid or glassy is brought about in the use of adhesives, solders and brazing metals. This aspect is considered in the paper by Dr. Crow. It has been suggested that chemical combination or mechanical interpenetration of the adhesive or solder and the surfaces which are to be united is essential to the making of a strong joint, but this appears to be negatived by exact experiments, in which care is taken to produce very thin films. Pure chemical compounds, both organic and inorganic, when melted and allowed to solidify in thin films between smooth surfaces of metal, give surprisingly high tensile strengths, triphenylcarbinol between polished steel plates giving 1·3 kg./mm.<sup>2</sup>, and Rochelle salt 0·9 kg./mm.<sup>2</sup><sup>35</sup>. Liquids give much lower values, and good lubricants are poor adhesives. In these instances there is no question of chemical action or of mechanical interpenetration, and the figures given represent true adhesion when the films are sufficiently thin, the adhesive pulling away from one or both metallic surfaces. With thicker films the value obtained represents the tensile strength of the adhesive, which is of a lower order. The thinner the film the higher the strength.

When one metal is electrolytically deposited on another, the adhesion is of a similar character. The operation being conducted at the ordinary temperature, there is no interpenetration, although subsequent heating may cause diffusion to a small extent. The older determinations of the degree of adhesion were made by depositing sufficient metal on a cylindrical bar to form a collar, the force necessary to pull off the collar being then measured. As electrolytic deposits are usually in a state of internal tensile stress, the conditions are like those of a shrunk-on collar, and a large force would be needed to separate the two metals even if there were no adhesion. This difficulty was overcome by Ollard,<sup>36</sup> who deposited nickel on the end of a rod in such a way that a true tensile test could be made. The adhesion between nickel and steel amounted to 30 kg./mm.<sup>2</sup>, this figure being a minimum, and the fracture tearing away part of the steel surface. The electrolytic nickel itself had a tensile strength of about 69 kg./mm.<sup>2</sup>. When the surface of the basis metal has been well cleaned, union is so perfect that the crystals of the electrolytic metal are continuous with those of the basis when the two metals are the same, as when copper is deposited on copper.<sup>37,38</sup> Such facts as these show that adhesion and cohesion are fundamentally the same.

9. Whilst the passage of foreign substances through solids may in some instances be attributed to the presence of minute channels, there is no doubt that true diffusion can also occur, it being a necessary condition that the diffusion substance shall be capable of entering into solid solution with the medium, if only to a limited extent. It would seem simplest to assume that the diffusing atoms displace those of the crystal step by step, occupying temporarily positions in the space lattice which they exchange for others as they pass through, but there are reasons for questioning this simple view. In metallic aggregates diffusion follows Fick's law, a recent example being

<sup>34</sup> Hardy and Nottage, *Proc. Roy. Soc.*, 1926, **112** A., 62.

<sup>35</sup> McBain and Lee, *Proc. Roy. Soc.*, 1927, **113** A., 606.

<sup>36</sup> E. A. Ollard, *Trans. Faraday Soc.*, 1925, **21**, 81.

<sup>37</sup> Huntington, *Trans. Faraday Soc.*, 1905, **1**, 324.

<sup>38</sup> Blum and Rawdon, *Trans. Amer. Electrochem. Soc.*, 1923, **44**, 305.

the loss of zinc on heating brass, when the zinc diffuses from the interior of the solid solution to the surface, where it escapes as vapour.<sup>39</sup>

When two metals are in contact, diffusion may take place in both directions, as when nickel diffuses into copper and copper simultaneously into nickel. When single crystals are used, diffusion is not observed.<sup>40, 41</sup> This has been confirmed by several workers. It is true that single crystals of iron are readily carburised, but the change is accompanied by great disturbance, and it has not been shown that the mass is still a single crystal at the end of the process. Hevesy has suggested<sup>42</sup> that step-by-step replacement does not occur, but that a preliminary loosening of the space lattice is necessary, the foreign atoms then travelling through the regions of looser texture, which may subsequently resume their ordered character. The facts concerning the electrolytic conductivity of crystalline salts and of such substances as quartz, on which there is an extensive literature, seem to confirm this view. A metal is hardened, that is to say its cohesion is increased, by the diffusion of a second element into it, so that the mechanism of diffusion in solids has a distinct bearing on the problem of cohesion in general.

### The Nature of Cohesion.

From what has been said above it will be seen that the simplest case of cohesion is that of a single crystal having a space lattice of a high degree of symmetry, such as rock salt. The tensile stress necessary to pull the crystal apart in a direction normal to a given crystal plane would be a physical constant of the highest interest. It should be different for each set of corresponding planes. Unfortunately, it is a matter of great difficulty to realise the conditions of the test, even approximately. In the first place, true single crystals are rare, either in nature or amongst artificial products. The evidence of X-rays, as well as that derived from experiments on deformation and fatigue, goes to show that apparently perfect crystals are aggregates of smaller masses having slightly varying orientations. This has been used as an explanation of the fact that when a crystal is deformed by slip, only a very small fraction of the number of available planes is actually concerned, the crystal deforming by the slipping of blocks of considerable and approximately equal thickness. This is, however, one of the many manifestations of periodicity in crystals, and it may be that it is related to the extraordinarily regular twinning of crystals of potassium chlorate,<sup>43</sup> and to the alternations in amethyst, effects which are unexplained, but which are not likely to be due to impurities. Ordinary metals consist of an aggregate of small crystals of random orientation, whilst the process of cold working brings about a certain degree of regularity, specific crystalline directions setting themselves parallel with the axis of deformation. The problem of cohesion in such masses involves that of the nature of the crystal boundary, whilst the hardening of both single crystals and aggregates by deformation leads to the question as to the nature of the change undergone by the space lattice, whether due to an equilibrium between elastic stresses in the planes of the lattice or to a more profound disturbance, ending in the production either of a vitreous phase or of a mass of fragments of mixed orientation.

One of the objects of the present Symposium is to bring together the views of physicists and engineers on the strength of materials. Another,

<sup>39</sup> Dunn, *J. Chem. Soc.*, 1926, 2973.

<sup>40</sup> Geiss and van Liempt, *Z. Metallkunde*, 1924, 16, 317.

<sup>41</sup> Hevesy and Obrutscheva, *Nature*, 1925, 115, 674.

<sup>42</sup> *Z. physikal. Chem.*, 1922, 101, 337.

<sup>43</sup> Lord Rayleigh, *Phil. Mag.* 1888 (v.), 26, 256; *Coll. Papers*, iii., 204.

more purely physical, is to discover whether any agreement can be reached as to the nature of the laws of cohesion in a homogeneous medium. Many attempts have been made to represent these laws by some simple mathematical expression. When the equation of van der Waals is written in the form,

$$P + \frac{a}{v^2} = \frac{RT}{v - b}$$

the first term represents the external pressure and the second the cohesion, both tending to reduce the volume, whilst the term on the right is called the intrinsic pressure, tending to increase the volume. The use of the expression  $a/v^2$  to represent cohesion has been common in researches on solids as well as liquids, and it was correlated with the hardness by Traube,<sup>44</sup> whose methods, however, involve several assumptions which are not justified. The history of the subject has been reviewed in the paper by T. W. Richards cited at the beginning of this survey, and in the Colloid Report by Edser which has been already mentioned, whilst the formulæ proposed for the internal pressure have been well reviewed by W. C. M. Lewis.<sup>45</sup> Many of the older writers assume that the force of cohesion varies inversely as the square of the distance, but the impossibility of this has been shown by many workers. Edser claims to have proved that the power must be higher than the fifth, and is probably the eighth. This point is dealt with by Professor Porter in this discussion.

Richards has shown that the equation of state for monatomic solids and liquids should contain four terms instead of three, the compressing forces being the external pressure  $P$  and the internal cohesive pressure  $\Pi$ , whilst the dilating forces are the internal distending or repulsive pressure  $\Pi_P$  and the thermal pressure  $P_\theta$ .<sup>46</sup>

The full expression, which is given and explained in Professor Richards' paper in the present discussion, has proved of value in calculating the compressibilities and other properties of solids. Since chemical and cohesive forces in solids are in all probability of the same kind, the determination of the compressibilities and coefficients of expansion of salts and comparison with those of the elements affords an interesting test of hypotheses of cohesion.<sup>47</sup>

Since so much of the experimental work on the cohesion of solids has been done on crystals of ionic structure, such as rock salt, it is natural that much attention should have been given to a prediction of the mechanical properties from electrical theory. This treatment of the subject is largely due to Thomson<sup>48</sup> and to Born,<sup>49</sup> and an important aspect of it is dealt with by Professor Lennard-Jones in his contribution. An ionic interpretation of slip in crystals was given by Stark,<sup>50</sup> but the difficulties in the way of a complete interpretation are very great. It must not be forgotten, also, that magnetic forces must be present in the space lattice, and that magnetic theory is as yet quite inadequate to deal with them.

<sup>44</sup> Traube, *Ber. deut. chem. Ges.*, 1909, **42**, 1594.

<sup>45</sup> Lewis, *Trans. Faraday Soc.*, 1911, **7**, 94.

<sup>46</sup> T. W. Richards, *J. Amer. Chem. Soc.*, 1926, **48**, 3063, developing ideas contained in papers from 1901 onwards.

<sup>47</sup> Richards, *J. Amer. Chem. Soc.*, 1925, **47**, 731.

<sup>48</sup> J. J. Thomson, "The Electron in Chemistry," Chap. V., London, 1923.

<sup>49</sup> M. Born, *Atomtheorie des festen Zustandes*, Berlin, 1923.

<sup>50</sup> J. Stark, *Physikal. Z.*, 1912, **13**, 585.

## MECHANICAL AND ELECTRICAL STRENGTH AND COHESION.

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The electrical theory of solids worked out by M. Born and his colleagues accounts in a satisfactory manner for the density, elasticity, dielectric constant and symmetry of crystals. In the case, however, of the absolute value of cohesion, the molecular forces when computed by the electrical theory exceed by many hundred times the strength observed in practice.

If we try, for example, to overcome the cohesive forces in rock-salt by mechanical tension, we actually find that the crystal can be broken at a stress of  $0.4$  kg./mm.<sup>2</sup>, whereas electrical theory predicts rupture at a stress of no less than  $200$  kg./mm.<sup>2</sup>.

If, again, we seek to destroy the crystal by electric forces, we actually observe the breakdown at a field somewhat below  $300,000$  volt/cm.; on the other hand, electrical theory leads us to the conclusion that fields of at least  $100,000,000$  volt/cm. are required to tear the ions out of the lattice and in this way to destroy the crystal.

With regard to mechanical strength, it may be possible to explain the discrepancy between the enormous cohesive forces and the small tensile strength, by supposing that the rupture of the crystal is not produced simultaneously across the whole cross-section. We can, for example, as proposed by Griffith, direct our attention to the rôle of minute cracks. The stress at the edge of such a submicroscopic crack would exceed by some hundred times the average stress, and would accordingly produce a growth of the crack. A gradual increase of the crack over the whole cross-section of the crystal has the same results as a simultaneous breaking down of the cohesive forces. It is evident that the first mechanism requires much smaller forces than the latter.

Sharp discontinuities in a well-formed single crystal are only to be expected on the surface. It can be supposed that such discontinuities do not take place on a fresh surface at once but appear gradually. It may be expected that the development of such cracks can be avoided by removing the surface quickly enough. Miss Lewitsky and I applied this idea in the following manner:—

We put a rock-salt crystal in hot water and studied the tensile strength of the crystal while its surface was continually dissolving. We found in fact that the parts of the crystal which were submerged had a much greater tensile strength than the dry portions. The crystal failed on the dry cross-section even when the cross-section of the submerged part was twenty times smaller than that of the dry. Finally, when the wet cross-section was, by continuous solution, reduced to a very small fraction of the dry one, the rupture of the submerged cross-section took place. In this way tensile stresses of about  $30$  kg./mm.<sup>2</sup> to  $160$  kg./mm.<sup>2</sup> were observed; those values are not too far from the theoretical value  $200$  kg./mm.<sup>2</sup>

Those experiments were open to the objection that at the moment of rupture the crystal might already be plastically deformed and that the high tensile strength measured in this way belongs to a strengthened polycrystalline body. In order to remove these objections we carried out the experiments in a different manner. We avoided the treatment of the surface with water, as the nature of this process is not known with certainty, and made use of the theoretically simpler case of a uniform instead of a unilateral tension.

A sphere of rock-salt was carefully cooled with liquid air and then suddenly plunged in hot water or fused lead. There arose a tension between the cold centre and the outside layer which reached in several seconds to its maximum value at the centre of the sphere. The maximum uniform tension is independent of the diameter of the sphere and reaches by plunging the sphere into boiling water, about  $25 \text{ kg./mm.}^2$ , and into fused lead about  $70 \text{ kg./mm.}^2$ . As the surface of the sphere is free, no radial tension can arise on the surface. Thus the state of the surface has little influence on the behaviour of the sphere. In this way the cracks do no damage and there is no necessity of avoiding them. There exists a tangential pressure besides the radial forces. This tangential pressure does not vanish at the surface, as do the radial forces, but it cannot involve a rupture at the surface. We found that so long as the sphere was heated uniformly, no rupture occurred in the sphere. Thus the rock-salt is not destroyed by a uniform tension as high as  $70 \text{ kg./mm.}^2$  or 7000 atmospheres, if only the action of the cracks at the surface is excluded by the peculiar distribution of the stress. We conclude from the experiment that cohesion in rock-salt is actually as high as is expected from the electrical theory. The very small tensile strength usually observed in crystals must thus be explained by the defects of the surface.

The discrepancy in regard to electrical strength was elucidated in a similar way. The small dielectric strength usually observed could be explained as arising from secondary effects; avoiding those effects we succeeded in discovering a 500 times greater strength in accordance with the theory. The chief causes of an early breakdown are as follows:—

1. The heat evolved by the current;
2. The production of new ions by the movement of some nascent ions (ionisation by collision);
3. Irregular field distribution (local over-voltage);
4. The spreading of cracks by mechanical tensions due to the field.

The two latter causes of the breakdown were investigated in this laboratory by A. Walter and L. Inge and by J. Horowitz and B. Pines, and their results are published in *Archiv. für Elektrotechnik*, 1927.

The first explanation of the breakdown was proposed by K. Wagner and has been much discussed by technicians. All dielectrics have a high and positive temperature coefficient of electrical conductivity. The heat evolved by the current increases the conductivity, increases the current and accordingly the amount of heat evolved. The temperature rises very quickly until a state of equilibrium is reached between the heat carried away by thermal conductivity and the heat supplied by the current. If the equilibrium temperature does not exceed the melting-point, this process involves a heating of the dielectric and a loss of energy only. If, however, the melting temperature is reached, melting and even evaporation result.

It is obvious that such an explanation of the breakdown process permits us to expect a strong dependence of the breakdown potential on temperature. The nearer to the melting-point is the original temperature of the dielectric,

the smaller the voltage which brings about breakdown. A computation made by W. Fock and N. Semenoff in our Institute and simultaneously by Regowsky and Kármán in Aachen, leads to the conclusion that the breakdown voltage must increase from the melting-point down to low temperatures as an exponential function and that the exponent of this law must be about half as great as that in the formula for electrical conductivity,

$$\log V_d = \frac{L}{T} + \beta \quad . \quad (1) \quad \log \sigma = - \frac{A}{T} + \beta \quad . \quad (2)$$

These and other conclusions of the heat-breakdown theory were very accurately tested and confirmed by A. Walter, N. Semenoff, and L. Inge on glass, rock-salt and porcelain at high temperatures. The particular result was that the breakdown voltage dropped to very small values of 50-100 volts at temperatures just below the melting-point. The experiments in general leave no doubt that at temperatures exceeding 200° C. the breakdown is caused by the heat evolved. Plotting the logarithm of breakdown potentials against reciprocal absolute temperatures, we find a straight line between 700° and 200° C., and its inclination is half as great as that of the logarithm of the conductivity (Fig. 1). At 200° C. the direction of the line is abruptly changed, and down to liquid air temperature the breakdown potential remains independent of temperature. It is evident that in this domain the cause of the breakdown has nothing more to do with the heat evolved or with melting; breakdown results in this region of temperature as soon as a field strength of some hundred thousand volts per cm. is reached.

My experiments dealing with electrical conductivity in crystals showed cases where fields a hundred times greater did not produce any breakdown. The current passing through calcite or through some other solid dielectrics alters the potential distribution inside the substance in such a way that the whole drop of potential becomes concentrated in the neighbourhood of one of the electrodes. The thickness of this layer was found to be 1 to  $10\mu$ , while the potential difference could reach some thousand volts, which means that fields of about  $10^7$  volts/cm. could exist there.

We found that the increase of the breakdown potential cannot be explained by the lowering of the conductivity, and we supposed that the main cause of this effect lies in the very small thickness of the sheet. In the same way that the fall of the breaking potential in the neighbourhood of the melting-point marks the breakdown by heat, so the increase of the breakdown potential in very thin sheets is evidence of ionisation by collision.

Let us consider for instance a dielectric where the applied electric field  $E$  is sufficient to produce ionisation by collision. In order to accumulate the necessary amount of energy the ion has to travel a distance  $\lambda$  under the action of the field and to pass the potential difference  $P$ . Denoting by  $D$  the thickness of the sheet and by  $V$  the applied difference of potential, we

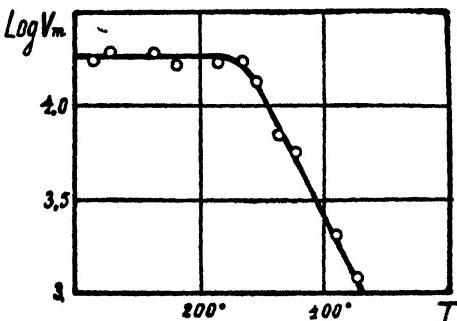


FIG. 1.

may expect that the number  $Z$  of ionising collisions which an ion suffers during its passage from one electrode to the other is

$$Z = \frac{D}{\lambda} = \frac{V}{P} \quad (3)$$

Every ionisation by collision doubles the number of ions. Thus the  $N_0$  ions starting on the one electrode produce on their way  $N$  ions and

$$N = N_0 e^Z \quad (4)$$

Considering the case when the ions are distributed uniformly throughout the dielectric with the density of the  $n_0$  ions per cm.<sup>3</sup>, we obtain for the average density  $n$  of the new ions,

$$n = n_0 \frac{V}{P} (e^{\frac{V}{P}} - 1) \quad (5)$$

So long as  $\frac{P}{V} = \frac{D}{\lambda}$  is sufficiently small, ionisation by collision has no important consequences other than an increase of the current and a distortion of the potential distribution.

If now  $\frac{D}{\lambda} = 5$ ,  $n = 20n_0$

For  $\frac{D}{\lambda} = 10$ ,  $n \approx 4000n_0$

and for  $\frac{D}{\lambda} = 20$ ,  $n = 10^8 n_0$

It is obvious that we reach a dangerous limit at about  $Z = 15$ . We can estimate the length of the path  $\lambda$  where the ions are accumulating their

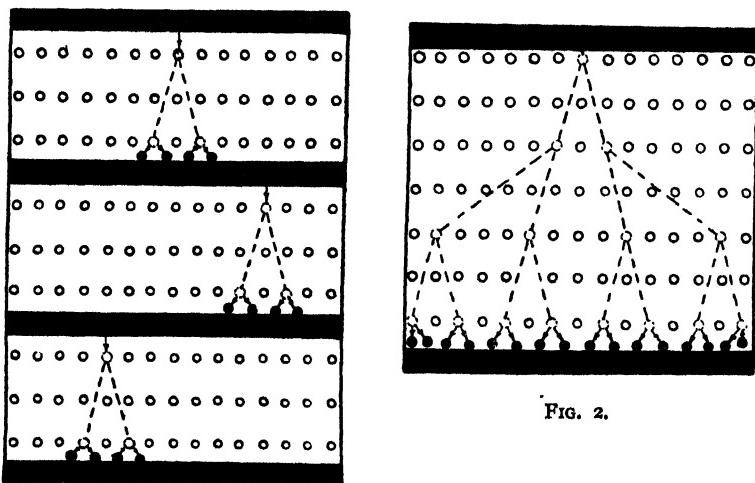


FIG. 2.

energy, as equal to about  $10^{-6}$  to  $10^{-5}$  cm., that is, to some hundreds of molecular distances. Thus if we have a sheet of dielectric of thickness  $D = 1$  mm., the number of ionising collisions is  $Z = \frac{D}{\lambda} = 10^4$  and the

number of ions newly produced  $n \approx e^{10000} n_0$ , it is then evident that, as soon as ionisation by collision starts, breakdown is inevitable.

In sheets which are sufficiently thick, compared with  $\lambda$ , breakdown occurs when a field is reached sufficient to produce ionisation by collision. The conditions are quite different in sheets thin enough compared with  $\lambda$ . The number  $n$  becomes here the most important factor. We may conclude that breakdown takes place when a sufficient average density  $n_k$  of ions is reached. Formula (5) shows that breakdown is involved at a certain value of  $\frac{V}{P}$ . If we consider first  $P$  as independent of  $V$  and  $E$ , we are drawn to the conclusion that the breakdown potential  $V$  is independent of the thickness  $D$ , while the average field strength  $E = \frac{V}{D}$  is inversely proportional to the thickness.

Experiments carried out by K. Smel'nikoff, T. Kurchatoff, and myself, on thin sheets of glass, mica, colophonium, picein, oil and benzene, led us to the conclusion shown in Figs. 3 and 4. Thus we have to consider

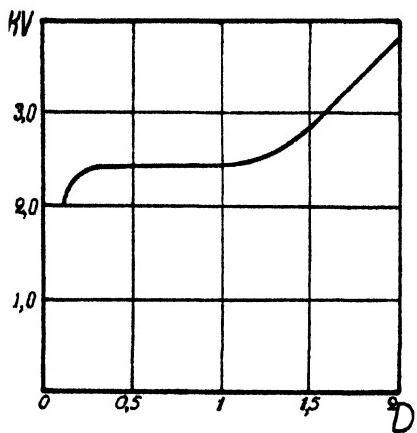


FIG. 3.

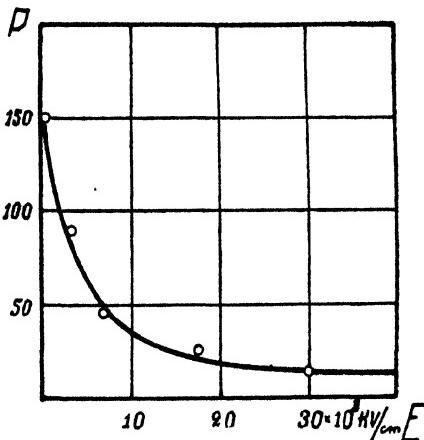


FIG. 4.

sheets exceeding  $0.5\mu$  as thick sheets, while for sheets thinner than  $0.5\mu$  formula (5) is valid. The dielectric strength is, however, only indirectly connected with the theory of collisions. The main supposition concerns the production of new ions increasing in an exponential manner with  $\frac{V}{P}$  or  $\frac{D}{\lambda}$ . But the current is given by the number of ions. We measured, for instance, the current  $I$  as a function of the field  $E$  and of the thickness  $D$ . Preliminary experiments have shown that it takes several seconds for the conductivity to be affected by the heat evolved. We proceeded to apply the field for  $0.1$  sec. only, with intervals of  $2$  sec., and gradually increased the field by equal steps. The corresponding currents were photographically registered by a string galvanometer. The results are given in Fig. 5. Up to the beginning of the ionisation by collision, which occurs at  $3 \times 10^5$  volt/cm., Ohm's law is fairly valid. The thicker the sheet, the more rapidly does the current increase after this limit is reached, according to the fact that

$$Z = \frac{V}{P} = \frac{ED}{P} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (6)$$

Every part of the curve permits us to determine  $P$  and  $\lambda$ . The curve corresponding to the previous density of ions,  $n_0$ , must become nearly horizontal after ionisation has begun. The relation between the current  $I$  corresponding to the field  $E$ , and the current  $I_0$  corresponding to the original density of the ions  $n_0$ , is a measure of the relative increase of the density of ions,

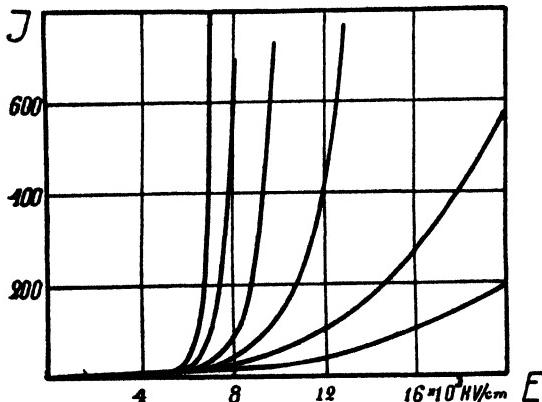


FIG. 5

$$\frac{I}{I_0} = \frac{n}{n_0}. \quad (7)$$

Formula (5) furnishes then the value of  $P$ . We conclude (Fig. 5) that  $P$  is a function of the field strength  $E$ ; in fact no other expectation was possible. The kinetic energy is accumulated on a path  $\lambda$  comprising many atomic distances.

The movement cannot proceed therefore without energy losses. The higher the field  $E$ , the shorter is the path  $\lambda$  and the smaller are the energy losses. A smaller potential difference  $P$  is required for reaching the necessary ionising energy  $eP_0$ .

$P$  and  $P_0$  are approaching equality at very high field strengths, the path  $\lambda$  amounts then to several atomic distances only.

In order to obtain a quantitatively correct theory we have to consider the space charge produced by the ionisation, as altering the distribution of the field.

In the domain of ionisation by collisions the mobility itself is no longer constant but becomes a function of the field strength. We reserve the necessary corrections and the analysis of the collision processes for a future detailed communication.

We now ask the following question:—How far can we raise the field we gradually proceed to thinner and

thinner sheets of dielectrics? We succeeded in preparing glass films down to about  $0.014\mu$  and mica sheets down to  $0.05\mu$ . At a thickness  $D = 0.2\mu$ , a field strength of about  $1.5 \times 10^8$  volt/cm. was reached; the thickness was then lowered 15 times but still the dielectric strength re-

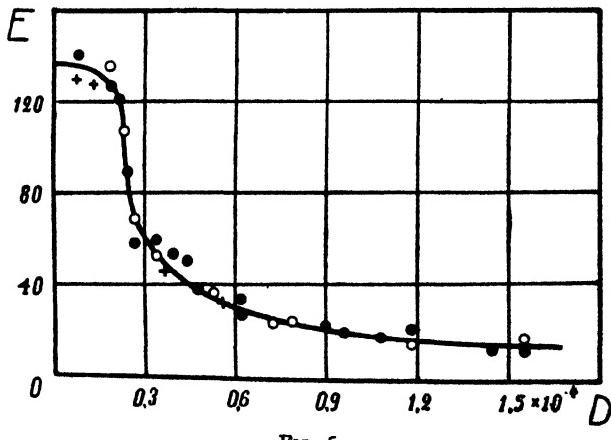


FIG. 6.

mained unaltered. This fact becomes quite evident from the logarithmic diagram (Fig. 7). Using electrodes made of different materials (brass, mercury, soot, water films, air ions), we discovered that this effect is fully independent of the electrodes and that the cause of the breakdown is to be looked for in the dielectric itself.

We suppose that this new region of breakdown, which is independent of the thickness, corresponds to the real dielectric strength of the substance dealt with. It is actually of the right order of  $10^8$  volt/cm. The elastic energy of an ion in a field of  $1.5 \times 10^8$  volt/cm. is equal to  $10^{-12}$  ergs., the kinetic energy of a gas mole-

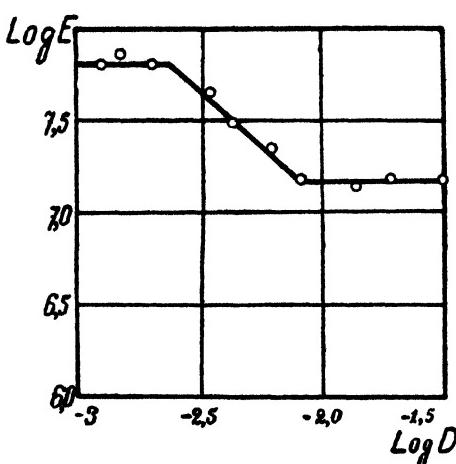


FIG. 7.

		Highest Field, $1.5 \times 10^8$ Volts Cm.	Usual Field, $3 \times 10^8$ Volts Cm.
1	Force exerted on an ion, $f = E \times \epsilon$ .	$2.4 \times 10^{-4}$ dynes.	$4.8 \times 10^{-7}$ dynes.
2	Attraction of the electrodes, $P = \frac{\epsilon E^2}{8\pi}$ . $\epsilon = 6$ .	$6 \times 10^{10}$ dynes cm. <sup>2</sup> = $6 \times 10^7$ atm.	$0.26$ atm. $= 2.6 \times 10^8$ dynes cm. <sup>2</sup> .
3	Specific energy per cm. <sup>3</sup> of the field, $u = \frac{\epsilon E}{8\pi}$ .	$6 \times 10^{10}$ ergs. cm. <sup>3</sup> = $1.4 \times 10^3$ cal. cm. <sup>3</sup> .	$2.6 \times 10^8$ ergs. cm. <sup>3</sup> $6.2 \times 10^{-3}$ cal. cm. <sup>3</sup> .
4	Elastic energy of an ion following from the frequency of residual rays, $u = \frac{\lambda^3 E^2 \epsilon^2}{4\pi^2 c^3 m}$ . $\lambda = 10\mu$ . $m = 7 \times 10^{-23}$ .	$u = 3 \times 10^{-12}$ ergs. corresponding to a temperature, $T = 1500^\circ$ abs.	$1.2 \times 10^{-18}$ ergs. $6 \times 10^{-30}$ abs.
5	Potential difference between two ions of the same sign over a distance $5 \times 10^{-8}$ cm. $V = E \times 2a$ .	7.6 volts	0.014 volts.
6	Tension between the lattice of positive ions and the interposed lattice of negative ions, $J = \frac{E \times \epsilon}{4a^2}$ .	$8 \times 10^{10}$ dynes cm. <sup>2</sup> = $8 \times 10^7$ atm.	$1.5 \times 10^7$ dynes cm. <sup>2</sup> = 160 atm.
7	Number of ions per cm. <sup>3</sup> bound on the electrode by the field, $n = \frac{\epsilon \times E}{4\pi\epsilon}$ .	$5 \times 10^{14}$ charges cm. <sup>3</sup> .	$10^{19}$ charges cm. <sup>3</sup> .

cule at  $1600^{\circ}$  abs. that is, the melting temperature of glass. There is no wonder that such a field is able to tear the ion out of the body.

The preceding highly instructive Table gives a digest of the data for the highest fields of  $1.5 \times 10^8$  volt/cm., together with the corresponding data for the highest fields of  $3 \times 10^6$  volt/cm. usually obtained. It is obvious that the possibility of obtaining such high fields in a solid body, fields which are comparable with chemical and cohesive forces, opens for us the way for a solution of some theoretical and practical problems. We are studying the dielectric constant, the elasticity, the residual rays, the Stark effect, and the surface tension in those fields. A new method of preparing insulators, condensers, etc., can be based on these results.

## DEFORMATION, RUPTURE, AND HARDENING OF CRYSTALS.

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A solid body subjected to a mechanical load alters its form. If on removal of the load the body returns to its original form it has been only elastically stressed, but if a part of the deformation remains it has been overstressed. Overstress may rupture the body or merely deform it; only when it is very brittle does rupture occur without previous deformation.

Deformation and rupture have been studied in very different materials; Griffith<sup>1</sup> has investigated amorphous substances, glass, and silica with success, whilst the very extensive experience of technical practice in regard to strength and working refers to crystalline materials, stones and metals; on the other hand the physical analysis of deformation and strengthening has been conducted in the first instance with single crystals, namely with salt crystals and especially with crystals of metals. In the present paper I am mainly concerned with investigations of metallic crystals, although on many points observations which have been made in technical practice are utilised.

### I. Monocrystalline Wires and Rods.

Since Laue's discovery of the refraction of Röntgen rays by crystal lattices the conception of a crystal has undergone a change for the physicist. When we speak to-day of a crystal we no longer think chiefly of the regular external form, the crystal faces and edges, which formerly constituted for us the distinguishing characteristics of a crystal. The most important feature is rather the crystalline structure made visible by these phenomena of refraction; that regular arrangement of the molecules which we designate as the crystal lattice. When, for instance, a sphere or rod is turned from a cube of rock salt, its crystal faces disappear, but since the sphere or rod has the same lattice structure as the cube from which it was made, we regard such a body also as a crystal of rock salt, and speak of it as a monocrystalline body. In virtue of their lattice structure monocrystalline bodies contain the crystal faces in latent form as specially closely

<sup>1</sup> Griffith, *Phil. Trans.*, 221, A. 163 (1921).

packed atomic net planes, which may be revealed also as cleavage planes or gliding planes, when the crystal is broken or deformed. Crystal edges are also present in the structure as closely set atomic lattice lines and are recognised, on breaking the body, as the edges of cleavage faces, or on deformation as directions of slip.

There are some monocrystalline bodies which do not merely lose their crystalline form by external working, but present themselves originally in forms which bear no relation to their crystalline structure. Such are the metallic single crystals. These are wires or rods of metal, which according to their structure are single crystals, but which do not show this in their external form. The latent crystal faces and edges reveal themselves when the body is plastically strained. Monocrystalline wires of zinc, which have been fully examined in collaboration with H. Mark and E. Schmid,<sup>2</sup> break at the temperature of liquid air along a crystal plane which is most often the basal plane ( $0001$ ) of the hexagonal lattice. The first prismatic plane ( $10\bar{1}0$ ) also occurs as a plane of fracture. Occasionally both planes appear, and then an edge is seen in which they meet, this being the latent crystal edge [ $10\bar{1}0$ ] (second diagonal axis). (See Figs. 1, 2, and 3.)

It has to be noticed that the planes of fracture in different monocrystalline wires of the same metal are differently inclined to the axis of the wire. This shows that in different wires the net-planes, and therefore the whole crystal lattice, are differently orientated to the axis of the wire. Since therefore in each wire the stress is applied to the lattice in a different direction it is evident that different planes may appear as planes of fracture. In general, that plane is favoured which is nearest to the transverse position.

The deformation of zinc crystals, which may be conveniently brought about by straining in tension at ordinary or elevated temperatures, also allows latent crystal faces to become apparent as slip planes, the traces of which are seen as slip lines on the outer surface of the crystal after elongation. (See Fig. 4.) A lattice line is also recognised as a direction of slip and can be identified crystallographically. This process of slip must now be examined somewhat more closely.

## 2. Slip in Single Crystals.

The results of tensile experiments on zinc crystal wires are illustrated by the wooden model shown in Fig. 5. The originally cylindrical specimen is drawn out into a band with elliptical section. This is due to slip along parallel planes, the traces of which are seen as slip lines in the form of ellipses on the outer surface of the band. (See Fig. 4.) A regular hexagon has been drawn on the slip plane in the model to show that in zinc the basal plane is the chief plane of slip, the plane which also appears by preference as the plane of fracture. The long arrow drawn on the slip-plane along the major axis of the ellipse gives the direction in which tension produces the greatest shearing stress. A closer examination of the model shows that slip does not take place in this direction but in that of the short arrow. This is manifested in the facts that the summit of the ellipse in a slip line does not lie in the middle line of the extended band, and that the breadth of the band is greater than the original diameter of the wire. This can be seen from the model and also from the photographs of the stretched crystal.

The cause of the deviation of the direction of slip from that of maximum stress lies, as may be seen from the model, in the crystalline structure.

<sup>2</sup> Mark, Polanyi, and Schmid, *Z. Physik*, 12, 58 (1922).

This is indicated on the model by the direction of the smaller arrow favoured by slip being parallel to the side of the hexagon; it is therefore a latent crystal edge, namely that lattice line representing the intersection of the basal plane with the first prismatic plane, having the crystallographic symbol  $[10\bar{1}0]$ .

The process of slip is thus not only limited by occurring in a crystallographically determined plane, even when this deviates appreciably from the plane of greatest shearing stress (which is always inclined at  $45^\circ$  to the axis of tension) but further by occurring in a crystallographically determined direction in that plane, which may differ from that of greatest stress. An influence of the direction of application of stress is to be noticed, in that of the three crystallographically equivalent  $[10\bar{1}0]$  lines, corresponding with the three directions of the hexagon in Fig. 5, that one becomes the direction of slip which makes the smallest angle with the direction of stress. This fact is also shown by the model.

The mechanism thus described, by which extension occurs, leads to a change in the orientation of the crystal lattice in relation to the axis of the monocrystalline wire. An examination of the model shows that the slip plane, that is, the basal plane, makes a progressively more acute angle with the axis of the wire as elongation increases. If the stretching could be continued in the same manner indefinitely, the basal plane would in time become parallel with that axis. Actually when zinc crystals are elongated, a position is reached in which the base makes an angle of 5 to  $6^\circ$  with the axis of the wire. Further, owing to the crystallographically determined direction of linear slip there is a line in the basal plane which becomes more and more nearly parallel with the axis of the wire. This is the  $[10\bar{1}0]$  direction, along which slip occurs.

With increasing deformation, therefore, goes a regular rotation of the lattice, leading to an arrangement in which the  $[10\bar{1}0]$  direction lies nearly parallel to the axis of loading. In a number of zinc crystals with varying orientation one can therefore bring about a parallelism of the lattices by stretching the crystals. Such a process occurs in the elongation of an ordinary microcrystalline wire of zinc. Here also each small crystal rotates in the same manner, its  $[10\bar{1}0]$  direction setting itself nearly parallel with the axis. Such an arrangement of the crystal structure, which on account of its resemblance with natural textile fibres is known as fibre structure, almost always occurs when metal wires are stretched, whereby different arrangements naturally arise according to the type of lattice.<sup>3</sup> With cadmium, which has a lattice like that of zinc, it is the  $[10\bar{1}0]$  direction which approaches the axis. With body-centred cubic metals, such as tungsten, molybdenum, and iron, it is the face diagonal of the cube. With face-centred cubic metals, such as copper, silver, and aluminium, two groups of crystals result, one with the cube diagonal and the other with a cube edge parallel with the axis of the wire. Tetragonal tin is an exception, not giving a fibre structure on stretching.

The correspondence between the fibre structure and the rotation of the lattice in the single crystal, which we have established in zinc, has also been confirmed for cadmium (E Schmid) and for a body-centred cubic metal, namely tungsten (F. S. Goucher).<sup>4</sup> For the face-centred cubic aluminium, however, there is a not yet explained abnormality. The orientation assumed by a single crystal is only exceptionally (mainly in hot deformation) the same as that observed in the fibre structure.<sup>19</sup> In the single crystal a final

<sup>3</sup> Ettisch, Polanyi, and Weissenberg, *Z. physik. Chem.*, 12, 58 (1922).  
<sup>4</sup> Goucher, *Phil. Mag.*, 6, 48, 229 and 800 (1924).

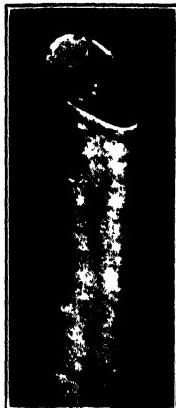


FIG. 1 ( $\times 10$ ).



FIG. 2 ( $\times 25$ ).

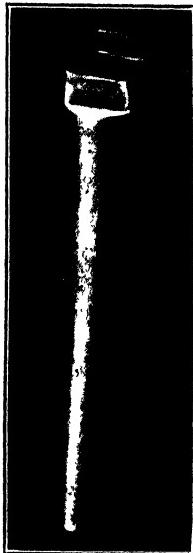
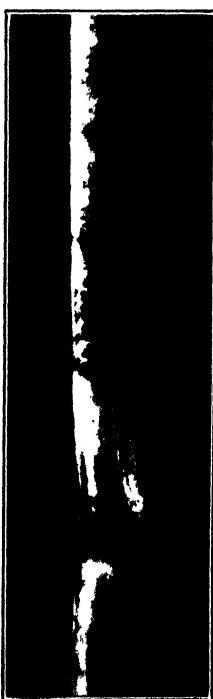
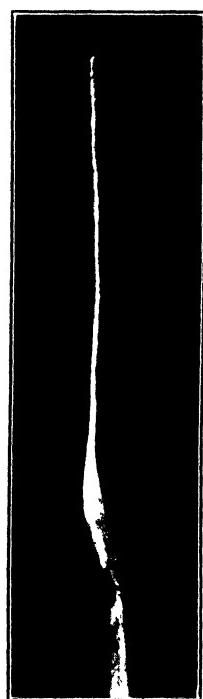


FIG. 3 ( $\times 2$ ).



(a)

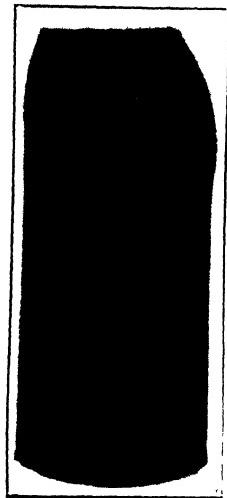


(b)

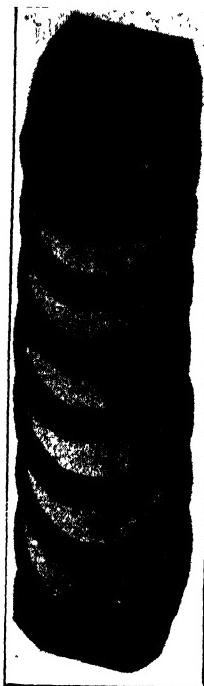


(c)

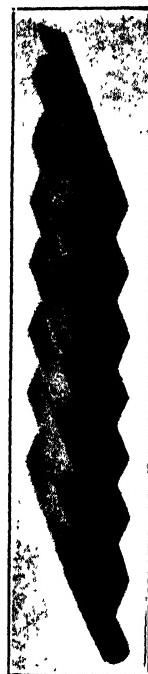
FIG. 4.—Extension of a zinc crystal. (a) Perpendicular, (b) parallel to the surface of the band. To the left of the arrow unstretched crystal approximately cylindrical. The breadth of the band is slightly greater than the original diameter. (c) Flongated zinc crystal with slip lines, unsymmetrical to the middle line of the band.



(a)



(b)



(c)

FIG. 5.—Model of elongation process. (a) Single crystal wire of zinc with cleaved basal plane. Long arrow — major axis of the ellipse of slip; under tensile stress this is the direction of maximum shear. Short arrow [1010] edge, direction of slip. (b) and (c) Front and side views of the model after elongation, showing band form and slip lines. The summits of the ellipses lie to one side of the middle line. The band is broader than the wire.



FIG. 6.—Extended tin crystal ( $\times 4$ ). The slip lines are fringed and discontinuous.



FIG. 7.—Bent slip planes in Tin ( $\times 16$ ).

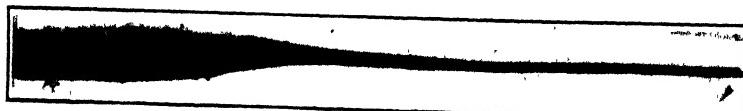


FIG. 9.—Partly extended tin crystal ( $\times 8$ ). Recrystallised.



FIG. 11.—Ridges at junction of crystals ( $\times \frac{2}{3}$ ). (Wetzel).

orientation is usually assumed in which the [112] direction lies near the axis, which is in accordance with the mechanism of deformation discovered by Taylor and Elam.<sup>5</sup> Why the microcrystalline wires should behave differently from the single crystals is not yet clear.

With reference to the work of Taylor and Elam it should be remarked that our representation of the elongation of single crystal wires is, through the choice of zinc as an example, somewhat too simple. The fact that in zinc one net plane has a preponderating tendency to slip, and that it does not occur repeatedly (there being only one basal plane in a hexagonal crystal) has the result that slip here takes place in preponderating degree on a single plane. Passing to cubic crystals, however, there is a competition between numerous equivalent planes and lines of slip (thus there are 4 octahedral faces and 6 cube face diagonals in aluminium) which is a determining factor. The final orientation towards which the lattice in the stretched wire is striving is here no longer such that one plane and one direction of slip lie in the axis of elongation. The final position is a stationary one, in which the rotations due to slip along the variously directed slip planes compensate one another.

Externally also the simultaneous slip along various planes has a result which differs from the example of zinc. Instead of the closed, well-marked slip lines which occur on this metal, the occurrence of different planes of slip produces intersecting, zigzag, and sometimes unrecognisably confused traces of slip. In Fig. 6 for instance, are seen the fringed slip lines of a tin crystal, due to simultaneous slip along different planes with the same direction slip (see Table I.).<sup>6</sup> It is probably owing to the same cause that Taylor and Elam have found in iron a definite direction of slip without being able to discover a plane of slip.<sup>7</sup>

### 3. Slip Planes, Slip Directions, Planes of Fracture, and Lattice Structure.

If in a crystal only certain planes and lines are observed to take part in slip, this may be supposed to be due to these having such easy slip that other planes and lines along which slip occurs less easily cannot manifest themselves. Only in such orientations of a lattice that the favoured planes and lines are exceedingly unfavourably placed (that is, nearly parallel with the axis of tension) do other directions come into play. On account of the presence of many equivalent planes and lines in cubic crystals it cannot happen in them that their position is so unfavourable that others come into action, but this probably happens in hexagonal and tetragonal crystals. In regular crystals therefore the principal plane and the principal direction of slip are always active, but in non-cubic crystals planes and lines of the second class may take part. This may be seen from the table, which also shows the following regularities:—

(1) In similar lattices (zinc, cadmium) and in lattices of the same type (such as face-centred cubic and body-centred cubic) the same planes and directions of slip are present.

(2) The most important planes and lines of slip are those which are most densely packed.

We shall return to the last point later in the section on the relation of the tenacity to the lattice theory. In regard to the first it should be

<sup>5</sup> Taylor and Elam, *Proc. Roy. Soc., A.* 102, 643 (1923).

<sup>6</sup> Mark and Polanyi, *Z. Physik*, 18, 75 (1923).

<sup>7</sup> Taylor and Elam, *Proc. Roy. Soc., A.* 112, 289 (1926).

DIRECTIONS AND PLANES OF SLIP AND PLANES OF FRACTURE IN METALS.\*

Metal.	Crystal System.	Direction of Slip.	Plane of Slip.	Plane of Fracture.	Most Densely Packed Lattice Line.	Most Densely Packed Lattice Plane.
Zinc <sup>2</sup> Cadmium	hexagonal	[1010]	(001) $S - 180^\circ = 0.12 \frac{\text{kg.}}{\text{mm.}^2}$ next probably (1010)	(001) $Z - 180^\circ = 0.18 \frac{\text{kg.}}{\text{mm.}^2}$ next (1010)	[1010]	(001) next (010)
Tin <sup>4</sup>	tetragonal	[001] next [101] followed by [111]	(100) and (110) apparently equal	[001] next [100] followed by [111] [101]	[100] next [111] [101]	(100) next (110)
Aluminium <sup>5</sup> Copper <sup>6</sup> Silver <sup>7</sup> Gold <sup>8</sup> Brass <sup>9</sup>	face-centred cubic	[101].	(111)	—	[101]	(111)
Tungsten <sup>4</sup> Iron <sup>10</sup>	body-centred cubic	[111]	?	(See close of Sect. 2)	[111]	(111)
Bismuth <sup>11</sup>	rhombohedral (nearly cubic)	[101] next probably [110]	(111) next probably (111)	$Z_{20^\circ} = 0.32 \frac{\text{kg.}}{\text{mm.}^2}$ next probably [1010]	[101] next [110]	(111) next (111)
Tellurium <sup>12</sup>	rhombohedral	probably [1010]	probably [1010]	$S_{20^\circ} = 0.22 \frac{\text{kg.}}{\text{mm.}^2}$ probably [1010]	[1010]	(001)

\* The figures against  $S$  and  $Z$  for zinc, bismuth, and tellurium are the values for the shear and tensile stresses at which slip on fracture occurs as determined by E. Schmid and his collaborators. (See Sect. 5.)

mentioned that recent observations have shown that the similar behaviour of similar lattices does not extend to the share in slip of different equivalent planes. Thus C. F. Elam<sup>8,9</sup> found that the slip in face-centred cubic crystals of brass differs from that in pure copper crystals. Also, according to E. Schmid<sup>10</sup> the fibre textures of silver, copper, and aluminium, although agreeing qualitatively, differ in the distribution of their small crystals between the two orientation groups (see above). It may be inferred that even in metals with the same structure the ratio of the slip and strengthening powers of different planes and lines is not the same. (See section 7.)

The rupture of crystals often occurs by increasing contraction without the appearance of a plane of rupture. The cases in which breaking of crystals has been observed are included in the table. Planes of fracture, like those of slip, belong to the most densely packed, or next most densely packed net-planes, and for zinc, bismuth, and tellurium are identical with the planes of slip, but this is not the case for iron or tungsten.

#### 4. Tenacity and the Lattice Theory.

One might suppose that the close relation of slip and fracture to the lattice structure, as apparent in the well-marked minimum of strength, both in shear and in tension, in the most densely packed atomic planes would indicate that the tenacity of crystals might be established on the theory of the lattice and might even be calculated therefrom. Unfortunately this expectation is not fulfilled.

This may be seen from the fact that rupture and slip do not take place in such a way that the forces which hold the crystal together are overcome by the applied force. Were this the case, the atoms, at the moment at which the crystal begins to yield plastically, would be in neutral equilibrium. The ductility in the direction of the critical stress would become infinite, in other words, the elastic modulus (or the modulus of shear) would become zero. That this does not happen, that on the contrary up to the limit of deformation there is scarcely any deviation from Hooke's law, shows that the mechanical failure of the metal must be regarded as "premature." It occurs far below the stress which would be theoretically necessary for the destruction of an ideal crystal lattice. This indirect conclusion may be confirmed by a computation of the theoretical tenacity and a comparison with that found in practice.<sup>11,12</sup> The theoretical value is several hundred kg./mm.<sup>2</sup>, as against 0·2 to about 0·5 kg./mm.<sup>2</sup> found for rock salt or zinc, so that the experimental value is less than one per cent. of the theoretical.

Attempts have been made to explain this contradiction by assuming some kind of loosening which accounts for the premature failure of crystals. Whilst formerly there was a tendency to assume accidental defects (cracks) as responsible (owing especially to the successful investigations of Griffiths on amorphous bodies), there is to-day an inclination rather to invoke thermal oscillations. The interesting discussion which has been proceeding in this direction on different assumptions between A. Smekal<sup>13</sup> and A. Becker<sup>14</sup> has not yet led to a definite decision. A complete lattice theory of rupture and slip will presumably also have to take into account the phenomenon of twinning, not hitherto referred to in this connection,

<sup>8</sup> Elam, *Proc. Roy. Soc.*, **112**, A, 289 (1926).

<sup>9</sup> *Ibid.*, **115**, A, 148 (1927).

<sup>10</sup> Pfeil and Edwards, *J. Iron Steel Inst.*, **109**, 129 (1924).

<sup>11</sup> Polanyi, *Z. Physik*, **7**, 323 (1921).

<sup>12</sup> Zwicky, *Physik. Z.*, **24**, 131 (1923).

<sup>13</sup> Smekal, *Physik. Z.*, **26**, 707 (1925); *Z. techn. Physik*, **7**, 535 (1926).

<sup>14</sup> Becker, *Z. techn. Physik*, **7**, 547 (1926).

since this process also occurs within the region of Hooke's law, that is to say "prematurely."

### 5. Tenacity with Varying Orientation.

In view of our powerlessness to deal at present with the central problem of tenacity, the investigation must limit itself to the laws of the actually observed tenacity, in the hope that these will serve for the ultimate solution of the problem. A fruitful method is the determination of the resistance to slip and rupture of metallic crystals having different orientations of the lattice in relation to the axis of the single crystal wire. In a series of extended determinations E. Schmid,<sup>15, 16, 17</sup> found for crystals of zinc, bismuth, and tellurium the law, surprisingly simple from the stand-point of the classical doctrine of tenacity, that each slip plane begins to slip at a definite shearing stress, independently of the magnitude of the tension perpendicular to that plane, and that further rupture occurs under a definite tension perpendicular to the plane of rupture, without being influenced by the shearing stress present at the same time *in* that plane. Schmid was able to show that the old determinations of the tenacity of rock salt prisms of different orientation by W. Voigt<sup>18</sup> also followed the same law. The law has also been verified by G. Sachs<sup>19</sup> for slip in aluminium.

### 6. Hardening. Strengthening towards Shear and Rupture.

A number of other, more qualitative regularities may be found by examining the effect, well known in practice, of the hardening by cold work in single crystals. A complication is introduced by the fact that the orientation of the crystal is changed by cold working, whereby its tenacity may be increased without any true change of properties merely because the stress necessary to produce a given tensile or shear stress in the principal plane of slip or rupture is increased by the rotation of the lattice. In collaboration with E. Schmid<sup>20, 21, 22</sup> however, it was found possible to eliminate this factor and to determine that the resistance to shear of tin and zinc crystals is increased many times by working (Shear strengthening). On the other hand it was shown in an investigation with G. Masing<sup>23</sup> that the tenacity of rolled zinc in liquid air may reach 200 times the value given by a single crystal under similar conditions (Tensile strengthening). Also, the greatly increased tensile strength of rock salt broken under water, observed by Joffé<sup>24</sup>, has proved to be a strengthening effect,<sup>25</sup> caused by the still entirely puzzling increase in the plasticity of wet rock salt.

Comparing with the results in the preceding section the facts may be summarised as follows: Cold working brings about a change in the crystal, by which slip and rupture set in less "prematurely," so that the tenacity approaches more nearly the theoretical value.

<sup>15</sup> Polanyi and Schmid, also Schmid and Georgieff, *Z. Physik.*, **36**, 759 (1926).

<sup>16</sup> Schmid and Wassermann, *Dissert of the latter*, Berlin (1927).

<sup>17</sup> Schmid, *Proc. Int. Congr. Appl. Mec. Delft*, 342 (1924).

<sup>18</sup> Sella and Voigt, *Ann. Physik*, **48**, 636 (1893).

<sup>19</sup> Karpov and Sachs, *Z. Physik*, **41**, 116 (1927) and **42**, 283 (1927).

<sup>20</sup> Polanyi and Schmid, *Verh. deutsch. physik. Ges.*, **4** (1923).

<sup>21</sup> Polanyi and Schmid, *Z. Physik*, **32**, 684 (1925).

<sup>22</sup> Schmid, *Z. Physik*, **22**, 328 (1924).

<sup>23</sup> Masing and Polanyi, *Erg. exakt. Naturw.*, **2**, 177, 1923 and *Z. Physik.*, **28**, 169 (1924).

<sup>24</sup> Joffé, Kirpitschewa, and Lewitzky, *Z. Physik*, **22**, 286 (1924).

<sup>25</sup> Ewald and Polanyi, *Z. Physik*, **28**, 29 (1924), and **31**, 776 (1925).

### 7. The Bent Crystal.\*

How, it may be asked, can the properties of a crystal be changed by cold working? It is evident that such a phenomenon calls for an addition to our conception of the lattice structure, so that the lattice of a deformed crystal must be thought of as differing from that of an undeformed one. I believe that the necessary modification can be found by a consideration of the bent crystal. We bend a single crystal prism at its middle point. How does such a change of shape take place? What is the condition of the lattice in the deformed portion?

As the mechanism of deformation, the slip-bending of Mügge<sup>26</sup> may be invoked, as has been observed in the bending of plates of gypsum. The layers which glide over one another do not remain parallel, but become curved in cylindrical fashion during bending about an axis which is perpendicular to the direction of slip (Fig. 7).

As regards the conditions in the bent part of the crystal, it must first be noticed that it is impossible that the lattice can remain unchanged. How the lattice has been modified in detail we do not know, but the following statements must hold good:—

1. The bent layers must be in a condition of elastic stress, tensile on the convex side and compressive on the concave side.
2. There must be a discontinuity between two bent layers, since a layer in tension is in contact with one in compression.

This condition is shown diagrammatically in Fig. 8, where two bent layers have been drawn. It will be seen that the surfaces of separation due to slip differ from ordinary grain boundaries in that here crystallographically similar faces are in contact. In view of this peculiarity such boundaries may be termed "internal surfaces of separation." It may be remarked that the elastic deformations are greatly exaggerated in drawing. They do not really exceed 0·5 per cent.

It may be asked whether this picture of the bent crystal makes it possible in any way to understand why such a crystal is hardened? I believe that this question may be answered in the affirmative.

The bent crystal must be hardened, because the lattice is broken along the inner surfaces of separation, and therefore all paths of slip (directions and planes of slip) which have to cross those surfaces are interrupted. It follows then that after slip in a system of parallel planes, further slip in any system which crosses these is hindered, so that the resistance to deformation is in this way increased. The objection may be raised, that this picture of hardening cannot apply, because not only is slip in directions which are not parallel with those in which the first slip occurred hindered, but also that in the direction of those planes. The answer is that a preferential strengthening of the initially "latent" slip planes is certainly present. This effect, which was first observed in tin,<sup>27</sup> and is there perhaps the most pronounced, was

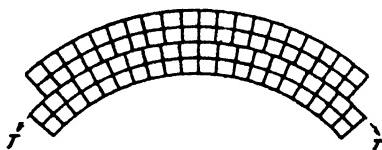


FIG. 8.—Elastically bent slip layers with an "internal surface of separation" along the curved line T-T.

\* The views given in this section and the next one were in essence first published in a lecture of the author to the Recrystallisation Committee of the Deutsche Ges. f. Metallk., Oct. 1922, and expanded by Masing and Polanyi, *Erg. d. exact. Naturw.*, 2, 177 (1923).

<sup>26</sup> Mügge, *Neues Jahrb. Miner.*, 1, 155 (1898).

<sup>27</sup> Polanyi, *Z. Kristallogr.*, 61, 49 (1925).

also seen in a lesser degree in aluminium and is conspicuous in the newer observations on brass.<sup>28, 29</sup> But whilst the preferential strengthening of the paths of slip of later origin is confirmed, it must be admitted that an exclusive strengthening of those paths is out of the question. To explain this, it must be supposed that from the very beginning slip does not take place exclusively along a single system of parallel paths, but that from the first other, smaller slips occur in directions crossing the main direction, these being of no importance for the gross deformation effects, but leading to an increase in the resistance in the main direction. It is improbable that slip is ever strictly confined to one parallel system of planes. By exact measurements G. Sachs and R. Kurnop<sup>19</sup> were able to detect the influence of several slip planes even from the beginning in the deformation of aluminium crystals. In zinc, also, where the preferential share of a single plane is most strongly marked, when the crystal is broken markings may be seen on the fractured surface, which are the traces of mutually crossing slip planes.<sup>2</sup>

It is further objected that the bending of a crystal is a special case of plastic deformation, with which such cold working as is represented by the purely parallel shearing of slip planes cannot be directly compared. But this objection is unfounded, as even in the most uniformly stretched crystal a curvature of the slip planes may be detected in the Laue diagram.<sup>30</sup>

Moreover, the explanation here offered deals with only one form of strengthening, namely that which increases the resistance to shear. The strengthening against rupture remains unexplained. One can at most refer to another equally puzzling phenomenon, namely that a fine-grained metal has a higher resistance to rupture than one with coarse grains or a single crystal.<sup>23</sup> Since during deformation internal surfaces of separation are produced, it is natural that the behaviour should be like that of a fine-grained metal.

### 8. Weakening of Crystals.<sup>31</sup>

Deformed crystals contain stresses and internal surfaces of separation. Their energy content is thus greater in two ways than that of the original crystal, by the state of stress and by the surface energy. Such a condition is a constrained one, and must tend towards a return to the normal condition, so that it might be expected that under suitable conditions a spontaneous return would be observed. In polycrystalline substances such a return of hardened material to the original condition with time, especially on raising the temperature (annealing) is well known, and it therefore seems well to bring it into relation with the change of a deformed crystal postulated above.

The first step, that of detecting spontaneous weakening of a single crystal, was successful. Two kinds of weakening of a stretched crystal wire could be detected. 1. A slow weakening, which is the more complete, the

<sup>28</sup> I conclude this from the fact that the first slip plane which forms goes beyond the point at which it would be stopped by a competing slip plane if the resistance to shear were equal.

<sup>29</sup> The observations by which E. Schmid (*Z. Physik*, **40**, 54, (1926)), was led to the conclusion that latent slip planes were less strengthened than those which were active at first, are to be interpreted in other ways according to Mathewson (*Amer. Inst. Min. Met. Eng.*, January, (1927)), and later to Schmid himself (*Z. Physik* in the press).

<sup>30</sup> Czochralski, *Z. Metallkunde*, **15**, 60, 126 (1923). Czochralski has given a different explanation of his observation. Later authors (E. Schiebold, G. Sachs), have confirmed these observations.

<sup>31</sup> This section is based principally on observations on tin-crystals made in collaboration with E. Schmid (first published *Verh. Deutsch. Phys. Ges.* **4**, (1923), later in detail, *Z. Physik*, **32**, 684 (1925)).

higher the temperature and the time during which it is exposed. 2. A second kind of weakening, which in tin always leads to the original strength without any definite intermediate stage. In the former case an alteration of the structure is not perceptible in a single crystal. This change is called "recovery." In the second case the wire consists after annealing of two or more crystals, so that a recrystallisation or division of grains has occurred. Since both recovery and recrystallisation also occur in polycrystals (only that the former has been only inferred, and not directly observed, on account of the complexity of polycrystalline specimens) the qualitative relation sought for between single crystals and polycrystals has been established.

If we further assume, as in the preceding section, that hardening is due to the internal surfaces of separation, then weakening must be due to healing of those surfaces of separation, by which the breaking up of the crystal disappears or is at least diminished, so that large masses of undisturbed lattice result. Such healing would not give rise to new crystal grains, but only to a change in those already existing. The more extensive the healing, the greater the softening.

The motive force of such a healing of the lattice must lie in the effort of the atoms along the surface of separation to return to their normal position. The actual movement due to these forces can only be of the order of magnitude of the interatomic distance, and therefore cannot give rise to any visible smoothing of the curved slip planes. The amount of the stresses in a crystal can thus only be lessened to a minute extent by healing, and it therefore remains to serve as the motive force for recrystallisation which occurs when the temperature is raised. Recrystallisation must be regarded as *an equalisation of stress, which does not take place by slip, but by grain growth.*<sup>22</sup>

It seems to me that certain important observations are in accordance with this hypothesis.

1. During recovery the curvature of the slip planes, as shown by X-rays, remains unchanged (G. Sachs).<sup>19</sup> On the other hand, recrystallisation, unless secondary stresses also take part, leads to a normal grain.

2. When a single crystal is deformed, the effect of the deformation is quite different, according as the deformation takes the form of an elongation, proceeding as in our model, or by rolling or hammering. Elongation produces much less hardening and much less tendency to recrystallise than rolling or hammering. For instance, a tin crystal, stretched to five times its length, does not recrystallise until just below its melting-point, at  $210^\circ$ , whilst an equally extended rolled specimen only requires  $60^\circ$ . The difference is due to the fact that in elongation the slip planes are only slightly bent and are almost plane in their final state, whilst in rolling or hammering the planes are crumpled, with corresponding accumulation of stress and abundant formation of internal surfaces of separation.<sup>21</sup>

3. If a partly elongated crystal be annealed, recrystallisation sets in at the point where the stretched and unstretched portions meet (Fig. 9). The greatest tendency to recrystallise is thus not caused by the maximum deformation, but by an intermediate amount. The peculiarity of this region lies in the fact that here the arrangement of the lattice of the original wire passes into that of the stretched band, so that the crystal is bent at this place. The strongly bent slip planes at this point are drawn so far during further elongation that no curvature visible to the eye remains.<sup>21</sup> That is to say,

<sup>22</sup> Naturally, either during recovery or at a temperature below that of recovery, a part of the internal stresses may be equalised. This will influence recrystallisation, but will not affect recovery. See G. Sachs and H. Shoji, *Z. Physik*, in the press.

in the course of elongation, whilst the slip planes are temporarily bent and then straightened, the tendency to recrystallise at the point of bending passes through a maximum, thus falling in spite of increasing deformation as the slip planes are again straightened. This mechanical straightening should be without influence on the internal surfaces of separation, so long as these are, as we have assumed, not made to disappear by rise of temperature. Thus hardening must continue to increase with increasing deformation, even when the curvature of the planes is vanishing. This is confirmed by the analysis of the curve of elongation; in spite of the increasing tendency to recrystallise the hardening continues to increase with the deformation.

This reversal of the tendency to recrystallise at the same time as the increase of hardening is probably the explanation of a simple experiment of J. Czochralski;<sup>33</sup> an aluminium rod is twisted, thus becoming hardened and at the same time increasing its tendency to recrystallise. On again untwisting the tendency to recrystallise is diminished but the hardening is further increased.<sup>34</sup>

4. Lastly, reference should be made to the very remarkable observation of E. Schmid<sup>35</sup> that during recovery not only does the increased resistance to deformation fall off (hitherto only this recovery towards shear has been considered), but also the increased resistance to rupture due to deformation disappears without recrystallisation. This effect, which it must be admitted is still entirely baffling, is in accordance with our suggestion that it is the internal surfaces of separation which are responsible for increased resistance towards rupture.

### 9. Single Crystals and Polycrystals.

Single crystals are thus, like polycrystals, hardened by deformation, both towards shear and tension. The hardened condition is seen to be, as in

polycrystals, one of constraint, which reverts to the normal condition on heating, either by recovery or by recrystallisation. This, however, is merely qualitative. Quantitatively there are great differences. Compare,

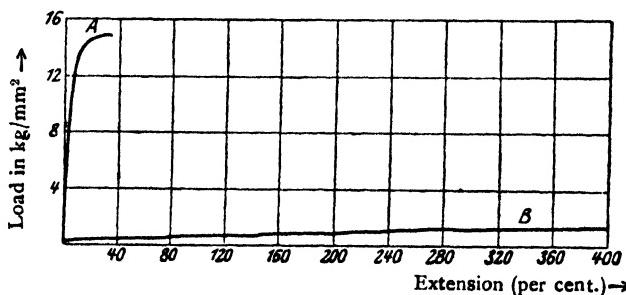


FIG. 10.—Extension curve of zinc.  
A. Annealed polycrystal. B. Single crystal.

compare, for instance, the extension curves of a single crystal and of a polycrystalline specimen in Fig. 10. It will be seen how much more rapidly the single crystal is hardened by extension. There is a similar difference in the tendency to recrystallise due to deformation; for equal deformation a single crystal needs a much higher temperature to bring about recrystallisation than a polycrystal. The cause of the difference must be, if our explanation

<sup>33</sup> Czochralski, *Proc. Int. Congr. Appl. Mec. Delft.* (1924), *Z. Metallkunde*, 17, 1 (1925).

<sup>34</sup> The latter point has been established by G. Sachs (*Z. Metallkunde*, 18, 209 (1926) who also confirmed the former.

<sup>35</sup> Schmid, *Z. Physik*, 32, 918 (1925).

be correct, that the internal surfaces of separation and the accumulations of stress in bent slip planes in the grains of the polycrystal are for equal deformation more numerous than in a single crystal. That this must be so will appear from an examination of a crystal grain closely surrounded by its neighbours; such a grain cannot possibly undergo normal deformation (stretching into a band, etc.), which alone makes possible the formation of a stretched crystal with plane surfaces of slip. The interruption at the grain boundaries constrains the deformation, bringing about a thorough crumpling in the interior.

It is to be expected that this constraint at the boundaries will be most strongly apparent in their immediate neighbourhood. The boundaries are in fact regions of great hardening. This is seen in the extension of a specimen consisting of two crystals, a ridge always forming at the boundary (Fig. 11). The boundaries are also the seats of preferential grain formation on recrystallisation, as was long ago shown by Chappel<sup>36</sup> and confirmed by experiments of specimens with two crystals.<sup>37</sup>

It is remarkable that, as pointed out by G. Sachs,<sup>19</sup> the difference in behaviour of single and polycrystals is smaller in cubic crystals. This is probably because here several slip planes and directions of slip are concerned, which cross one another and so cause more rapid strengthening.

#### **10. Position of the Main Problems.**

The geometrical mechanism of the deformation of crystals seems to be in agreement with earlier mineralogical investigations and to have been explained in essentials. On the other hand, the question as to the atomic basis of slip, fracture, and twinning seems to me to be unexplained. These three phenomena are closely inter-connected, and can only be explained together.

A picture of hardening may be made which starts from the condition of the bent lattice, and contains only the essential elements. This picture serves to explain some of the main features of hardening, recovery, and recrystallisation. Admittedly there are many things which are not explained, or only with difficulty, by this picture. Thus the change in the magnetic and electrical constants on deformation, the increase in the tendency for rock salt to become coloured by sodium vapour (Pribram and Smekal); the influence of water on the plasticity of rock salt, etc. Perhaps one or other of these phenomena may point to the alterations or additions which may be required to make the conception perfect.

<sup>36</sup> Chappel, *J. Iron Steel Inst.*, **89** (1914), I.S. 460.

<sup>37</sup> The argument of this section is further developed in the paper of Polanyi and Schmid, *Z. techn. Physik*, **5**, 580 (1924).

# PLASTICITY PROBLEMS IN METALS.

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The laws of crystallography are decisive in describing the processes of deformation in single crystals. On the other hand the phenomena in crystalline aggregates can at present but seldom be given an explanation on crystallographic methods. A series of effects observed in the deformation of metals can only be explained by treating the materials as homogeneous and isotropic wholes and the calculations can be carried out up to a certain limit by simple steps.

(1) A well-known phenomenon is the development of a neck in tensile tests as is apparent in Fig. 1 in an aluminium crystal and in Fig. 2 in a polycrystalline rod. This shows that a rod of high melting metal stretches under increasing load uniformly along its whole length, and that after maximum load has been reached the rod begins to contract laterally at one or more places.

Now, under homogeneous tensile stress the highest load should coincide with the beginning of contraction.<sup>1</sup> For, as long as the load increases, every cross-section of the rod is stretched, because any section that would stretch more than another becomes harder than the less stretched one. As soon, however, as the load falls off, the deformation is confined to a limited range of cross-sections.

The beginning of lateral contraction can be fixed experimentally by the relation between elongation and reduction of area,<sup>2</sup> or in a rod after fracture, by the extension of the uniformly elongated portion,<sup>3</sup> provided that the extended part remains partly cylindrical.

The point of maximum load can be experimentally determined only with difficulty since, with increasing elongation, the load usually remains constant for some time. The condition for maximum load

$$\begin{aligned} P &= s \cdot f = \text{maximum} \\ dP &= ds \cdot f + s \cdot df = 0 \end{aligned} \quad \dots \quad (1)$$

where  $f$  is the cross-section in question and  $s$  the stress therein can, however, be so written that the point of maximum load in the stress-cross-section curve (Fig. 3) can be readily fixed by graphic methods.<sup>4</sup> With

$$\tan \alpha = \frac{ds}{df} = - \frac{s' - s}{f} \quad \dots \quad (2)$$

<sup>1</sup> Considère, *Mémoire sur l'emploi du fer et de l'acier*, Paris, 1885; Die Anwendung v. Eisen u. Stahl bei Konstruktionen, Vienna, 1888; Ludwik, *Elemente der tech. Mechanik*, Berlin, 1908.

<sup>2</sup> Kurnop and Sachs, *Z. Physik*, 41, 116 (1927).

<sup>3</sup> Saeftei and Sachs, *Z. Metallkunde*, 17, 158 (1925).

<sup>4</sup> v. Moellendorff and Czochralski, *Z. V. d. I.*, 57, 931 (1913); Körber, *Mitt. K.-W. I. f. Eisenforschung*, 3, 2, 1 (1922); Sachs, *Ber. V. d. Eisenhüttenrente, Werkstoffausschuss*, 58 (1925).

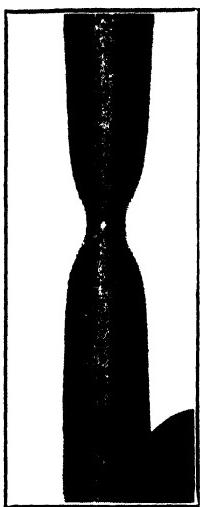


FIG. 1.—Contraction of an aluminium crystal.

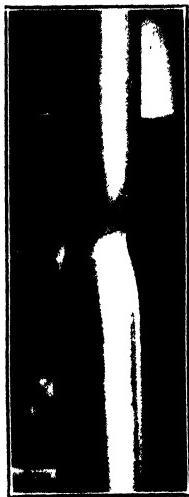


FIG. 2.—Contraction of a copper rod.



FIG. 15.—Drawn brass rod split after one day in 10 per cent. mercuric chloride solution.



FIG. 9.—Compressed iron cone recrystallised at  $830^{\circ}$  ( $\times 2$ ).

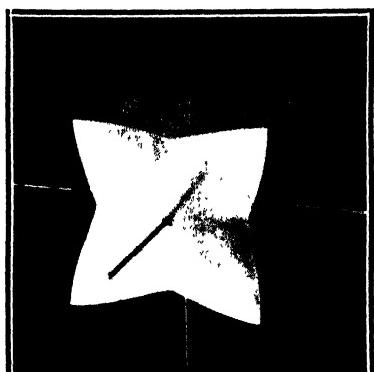


FIG. 19.—Aluminium crystal (unchanged).

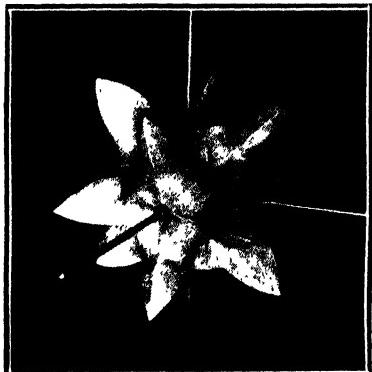


FIG. 20.—Aluminum crystal (stressed).  
[To face page 84.]



where  $s'$  is the intercept of the tangent on the line  $f = 0$  it follows for the stress at the point of maximum load stress,  $s_{11}$

$$-\frac{s'_{11} - s_{11}}{f_{11}} = -\frac{s_{11}}{f_{11}} \quad \dots \quad \dots \quad \dots \quad (3)$$

$$s_{11} = \frac{s'_{11}}{2} \quad \dots \quad \dots \quad \dots \quad (4)$$

In the stress-cross-section curve, Fig. 3, the point of maximum load stress can therefore be fixed by considering that the tangent at this point cuts the ordinate  $f = 0$  at a stress twice that at the point of maximum load.

In practice the calculated maximum load corresponds as a rule to an elongation somewhat less than that at which contraction begins<sup>2, 4</sup>; the reason is to be sought in the disturbance of homogeneity.

Lateral contraction in ductile materials occurs under rotary loading just as under tension. The behaviour of a rotating ring under the influence of centrifugal force can be computed just as in the tensile test.<sup>5</sup>

(2) Bending and torsion experiments provide another problem. Whenever plastic deformation occurs under such loading, the true stresses in the outer layer remain below those calculated from elastic theory. Since this fact is not usually taken into account, there are frequently to be found in the literature bending and torsional strengths which are too high. However, as Eugen Meyer<sup>6</sup> first showed for bending,<sup>7</sup> it is possible to deduce, by making simplifying assumptions, the more exact variation of stress from the moment. Conversely the stress-strain curves can be used to construct the curves of moments.

If a torsion experiment<sup>8, 9</sup> be made on a cylinder of radius  $a$ , and the relation of the shearing stress  $\tau$  to the specific shear  $\gamma$  is known —e.g. from a tension experiment—the specific shear can be taken as proportional to the distance  $r$  from the axis:

$$\gamma = r\delta \quad \dots \quad \dots \quad \dots \quad \dots \quad (5)$$

where  $\delta$  is the specific angle of torsion. The moment of torsion is then:

$$M = \int_{r=0}^{r=a} \tau \cdot df \cdot r = \frac{2\pi}{\delta^3} \int_0^a \tau \cdot \gamma^3 \cdot d\gamma \quad \dots \quad \dots \quad (6)$$

<sup>8</sup> László, *Z. angew. Math.*, 5, 281 (1925); *Maschinenbau*, 5, 210 (1926). 1

<sup>9</sup> Meyer, *Physikal. Z.*, 8, 827 (1907); *Z.V.d.I.*, 52, 167 (1908).

<sup>7</sup> See also, Bach and Baumann, *Elastizität u. Festigkeit*, Berlin, 1924, 271; Herbert, *Z.V.d.I.*, 54, 1387 (1910); Ono, *Mem. Coll. Engin. Kyushu Imp. Univ.*, I, 111 (1915).

<sup>8</sup> Prandtl, *Z.V.d.I.*, 54, 1388 (1910); Ludwik, *Elem. d. techn. Mechanik*, Berlin, 1909, 31; Ono, *Mem. Coll. Engin. Kyushu Imp. Univ.*, I, 195 (1917); Ludwik and Scheu, *Stahl u. Eisen*, 45, 373 (1925).

<sup>9</sup> Bader and Nadai, *Z.V.d.I.*, 71, 317 (1927).

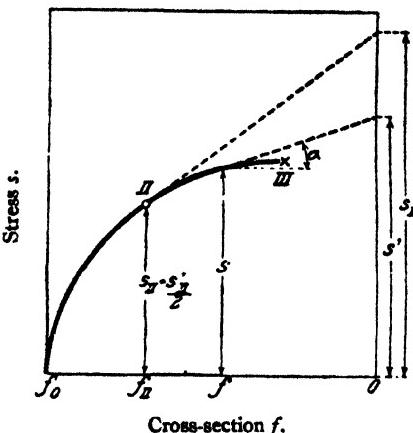


FIG. 3.—Calculation of maximum load.

The moment of torsion for a known twist is thus equal to the moment of inertia of the surface of the  $\tau$ - $\gamma$  curve up to the point  $\gamma = \gamma_a$  on the  $\tau$  axis multiplied by  $\frac{2\pi}{8^3}$ .

By differentiation of the moment :

$$\frac{d}{d\delta} (M\delta^3) = 2\pi\tau_a \cdot a^3\delta^2 \quad . . . . \quad (7)$$

we obtain

$$\tau_a = \frac{3}{2\pi a^3} \left( M + \frac{\delta}{3} \cdot \frac{dM}{d\delta} \right) \quad . . . . \quad (8)$$

Equation 8 makes it possible to ascertain the required maximum shearing stress  $\tau_a$  for each moment of torsion  $M$  by simple graphical means.

More complicated cases of torsion and shear strain can also be approximately treated mathematically<sup>10</sup> if it is assumed that after reaching the elastic limit the material flows under constant stress. The stress-strain diagram of such an "ideally plastic" material has the characteristic appearance of Fig. 4.

The solutions may be rendered very obvious, as the shear stress under

partly elastic and partly plastic loading in a cross-section is proportional to the slope of a membrane under internal pressure, in contact with a surface erected on that section, corresponding with the slope of a heap of powder in repose. According to the experiments of Bader and Nadai the flow-figures of twisted iron rod of different section take forms which correspond closely with the slope of such heaps.<sup>9</sup>

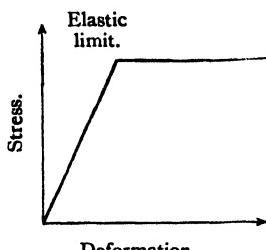


FIG. 4.—Stress-strain curve of an ideally plastic material.

(3) For the determination of the stress-strain

conditions of more complex processes Prandtl<sup>11</sup> has made use of the idea that a state of equilibrium is set up after the commencement of

plastic deformation. Assuming a stress-strain curve such as Fig. 4 we can, for instance, treat mathematically the impression of a rigid punch as in a hardness test. In doing this we make the assumption, which is not further examined, that under the punch the plastic region corresponds to the hatched portions of Fig. 5. The gradual transition from purely elastic conditions to the state of plastic equilibrium cannot be followed. It now follows that there arises in a horizontally limited body in the plastic condition a shearing stress as large as in the case of an ordinary compression specimen if the compressive loads are in the ratio

$$\left( 1 + \frac{\pi}{2} \right) : 1 = 2.57 : 1.$$

Considerations of elastic theory give, however, for a horizontally limited body under equally distributed compressive load, the same shearing stresses as in the case of compression when the compressive loads are in the ratio

<sup>10</sup> Nadai, *Z. angew. Math.*, **3**, 442 (1924); Trefftz, *ibid.*, **5**, 64 (1925).

<sup>11</sup> Prandtl, *Nach. Ges. Wiss. Göttingen, Math. Phys.* (1920), 74; *Z. angew. Math.*, **1**, 15 (1925); *ibid.*, **3**, 401 (1923), *Proc. Int. Congr. App. Mech.* (1924), 43; Hencky, *Z. angew. Math.*, **3**, 241 (1923), *Z.V.d.I.*, **69**, 695 (1925); Nadai, *Z. Physik*, **30**, 106 (1924); v. Mises, *Z. angew. Math.*, **5**, 147 (1925); Knein, *ibid.*, **6**, 414 (1926).

$\frac{\pi}{2} : 1 = 1.57 : 1$ .<sup>12</sup> According to recent experiments we can still assume that the flow under such conditions of loading as in the case of an impression like Fig. 5, where the middle principal stress lies somewhere between the two others, will occur at a shear stress  $1.155$  times as large as the uniaxial stress in an ordinary compression experiment.<sup>13</sup> Therefore the flow in horizontally limited bodies must also begin under compression stresses  $1.155 \times 1.57 = 1.82$  times as large as in the case of compression experiments.

Experiments on iron<sup>14</sup> gave, with sufficiently large test pieces, ratios between  $1.75$  and  $2.07$ , but the higher value was obtained with a punch only  $1$  mm. broad and  $20$  mm. long and is therefore not to be depended upon.

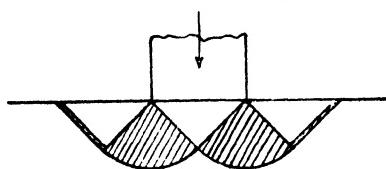


FIG. 5.—Plastic region (hatched) of a punch impression (Prandtl).

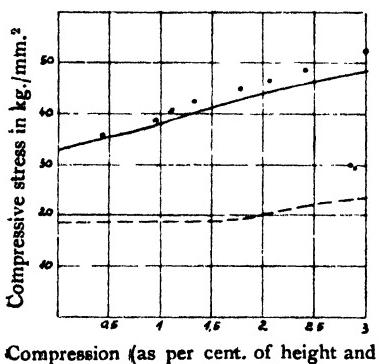


FIG. 6.—Pressure experiments on iron.

— — — Compression experiment.  
· · · · · {Impression} observed.  
— — — {experiment} calculated.

corresponding to Figs. 7 and 8

$$v = \int_{r=0}^{r=a} dv = \int_{\alpha=0}^{\alpha=\pi} \epsilon \cdot \frac{da}{\sin^2 \frac{\alpha}{2}} \quad \dots \quad \dots \quad \dots \quad \dots \quad (9)$$

where  $\epsilon$  is the aforementioned compression for the shearing stress.

$$\tau = \frac{P}{\pi} \cdot \sin \frac{\alpha}{2}^{15} \quad \dots \quad \dots \quad \dots \quad \dots \quad (10)$$

As expected the experimental points in Fig. 6 diverge from the calculated curve with increasing deformation, in the direction of higher stress, since

<sup>12</sup> Nadai, *Z. angew. Math.*, 1, 20 (1921).

<sup>13</sup> Hencky, *Z. angew. Math.*, 4, 223 (1924); Nadai, *Ber. V. d. Eisenhüttenleute, Werkstoffausschuss*, 56, 1925; Lode, *Z. Physik*, 36, 913 (1926); Schleicher, *Z. angew. Math.*, 6, 199 (1926); Ross and Eichinger, *Schweiz. Verb. Mat. Prüf.* (1926).

<sup>14</sup> Sachs, *Z. tech. Physik*, 8, 132 (1927).

<sup>15</sup> Ludwik, *Elemente tech. Mech.* Berlin, 1909; Sachs, *Mech. Techn. d. Metall., Leipzig* (1925), 54; Ludwik and Scheu, *loc. cit.* (ref. 8).

generally in the case of inhomogeneous deformation an increased resistance is to be expected on account of redistribution of stress.

The permissibility of the assumption of a distribution of stress according to elastic theory is further supported by recrystallisation experiments and determination of flow figures. Fig. 9 shows, for example, within the limits of the recrystallisation zone the circular formation of the curves of equal shear in a section demanded by theory.

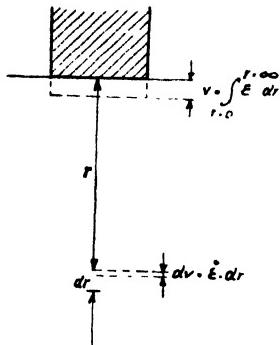


FIG. 7.—Calculation of stress-depth of impression curves.

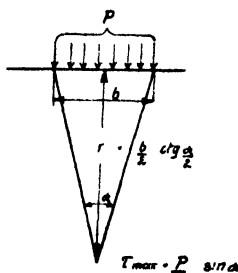


FIG. 8.—Shearing stress in impressed specimen.

The recrystallisation zone has nearly the same shape in a compressed cone as in an impressed horizontally limited body.

(4) Further work, moreover, has been undertaken in order to follow the flow of plastic masses.<sup>16</sup> Rigid treatment of the process leads, however, to complicated equations whose meaning and practical application cannot at present be seen.

By the introduction of rough approximations, nevertheless, examples such as rolling<sup>17</sup> and drawing<sup>18</sup> can be treated very simply. It is specially worthy of note that the different assumptions all lead to very similar results.

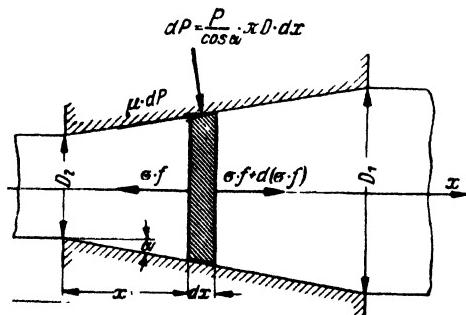


FIG. 10.—Calculation of forces required for drawing.

The shape of broken necked test-pieces can be deduced from the fact that the shearing stress must be uniform at all parts.<sup>19</sup>

To evaluate the forces necessary for drawing wire we make the following assumptions (Fig. 10):—

(1) The axial tension  $\sigma$  is distributed uniformly over every cross-section  
 $f = \frac{\pi D^2}{4}$  of wire which is being drawn.

<sup>16</sup> v. Mises, *Nach. Ges. Wiss. Göttingen, Mat. Phys.*, 582 (1913); Hencky, *Z. angew. Math.*, 5, 115 (1925); *Z.V.d.I.*, 69, 1253 (1925); Nadai, *Z. Physik*, 30, 106 (1924).

<sup>17</sup> v. Kármán, *Z. angew. Math.*, 5, 139 (1925); Dresden, *Z. angew. Math.*, 5, 78, 1925; 6, 176 (1926); Siebel, *Z. angew. Math.*, 6, 174 (1926).

<sup>18</sup> Becker, *Z. tech. Physik*, 6, 298 (1925); Siebel, *ibid.*, 7, 325 (1926); Sachs, *Z. angew. Math.*, 7, 235 (1927).

<sup>19</sup> Siebel, *Ber. V. d. Eisenhüttenleute, Werkstoffausschuss*, 71, 1 (1925).

(2) The pressure  $\rho$  on the draw-cone and the mean tension  $\sigma$  are principal stresses.

(3) In the region undergoing flow the shear stress is constant:—

$$\sigma + \rho = K . . . . . \quad (11)$$

where  $K$  is the limit of flow of the material and in practice can be put equal to the ultimate strength (or yield point) of tensile tests. Further, let  $D_1$  and  $D_2$  be the diameter of the initial and final cross-sections,  $x$  the axial co-ordinate (positive in the direction of increasing cross-sections),  $\alpha$  the angle of inclination of the draw-cone, and  $\mu$  the coefficient of friction. According to Fig. 10, then, the equilibrium condition for a small element of volume  $f \cdot dx$  is:

$$d(\sigma \cdot f) + dP(\sin \alpha + \mu \cos \alpha) = 0 . . . . . \quad (12)$$

In view of the fact that the cross-section  $D_2$  takes no stress we have:—

$$\frac{\sigma}{K} = \left( 1 + \frac{\tan \alpha}{\mu} \right) \left[ 1 - \left( \frac{D_1}{D_2} \right)^2 \cdot \frac{\tan \alpha}{\mu} \right] . . . . . \quad (13)$$

When

$$\frac{D_2^2}{D_1^2} = \frac{f}{f_1} = 1 - q,$$

and neglecting terms of the higher order of  $q = \frac{f_1 - f}{f}$  the equation becomes

$$\frac{\sigma}{K} = \left( \frac{\mu}{\tan \alpha} + 1 \right) \frac{f_1 - f}{f} . . . . . \quad (14)$$

The practical applicability will depend upon how far the assumptions which have been made will fit. An approximately uniform deformation of the whole cross-section occurs only when there is considerable reduction of area. The direction of the pressure diverges so much the less from the radial direction as the friction and the angle of drawing are less. A coincidence between calculation and experiment is therefore only to be expected for a small angle of inclination of the draw-cone and large change in cross-section.

(5) A technically important question is the evaluation of the internal stresses which remain in the material after a process of deformation. This proposition can be treated mathematically<sup>20</sup> and in several simple cases can be solved.<sup>21</sup>

For the estimation of stresses in drawn and rolled sections, however, there is no method of calculation. The stresses in plates can be estimated experimentally by the method used by Heyn and Bauer<sup>22</sup> for rods, wherein layers are planed off both sides of strips cut from the plate and the alteration in length is measured.

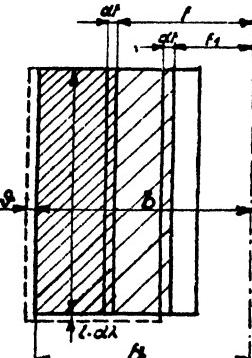


FIG. 11.—Calculation of internal stresses in rods and tubes.

<sup>20</sup> Haar and v. Kármán, *Nach. Ges. Wiss. Göttingen, Mat. Phys. Klasse*, 204 (1909); Hencky, *Z. angew. Math.*, 4, 223 (1924); *Proc. Int. Congr. App. Mech.* (1924), 312.

<sup>21</sup> A. and L. Föppl, *Drang u. Zwang*, 2, München and Berlin (1920), 297; Nadai, *Z. Physik*, 30, 106 (1924); *Z. angew. Math.*, 3, 442 (1924).

<sup>22</sup> Heyn and Bauer, *Int. Z. Metalllogr.*, 1 (1910), 16; *Stahl u. Eisen*, 39, 760 (1911); Heyn, *ibid.*, 32, 209 (1912); *Mitt. Materialprüfungsamt*, 35, 1 (1917).

In the case of a rod or tube, however, the measurement of two deformations is necessary for a complete understanding of the stress distribution. The rod is bored out in stages from the inside, so that the change in length  $\lambda$  and in thickness  $\delta$  (Fig. 11) can be measured.<sup>23</sup> In the process of removing a differential layer of cross-section  $df$  (where the tubular section is written as  $f$ ), the changes of specific length and thickness correspond to  $d\lambda$  and  $d\delta$ . From considerations of elasticity we get, for the outer skin  $f_b$  of the cylinder, the longitudinal stress  $ds_b$  and the tangential stress  $dt_b$ —

$$\left. \begin{aligned} ds_b &= \frac{E}{1 - \mu^2} (d\lambda + \mu d\delta) \\ dt_b &= \frac{E}{1 - \mu^2} (d\delta + \mu d\lambda) \end{aligned} \right\} . . . . . \quad (15)$$

where  $E$  is the modulus of elasticity and  $\mu$  Poisson's constant. At the place  $f$ , the longitudinal stress  $ds$  can be taken equal to  $ds_b$ , and according to equations for a thick-walled cylinder the tangential and radial stresses respectively are, from (15)—

$$\left. \begin{aligned} dt &= \frac{E}{1 - \mu^2} \cdot \frac{f_b + f}{2f} (d\delta + \mu d\lambda) \\ dr &= \frac{E}{1 - \mu^2} \cdot \frac{f_b + f}{2f} (d\delta + \mu d\lambda) \end{aligned} \right\} . . . . . \quad (16)$$

By boring out to the cross-section  $f$  the longitudinal, tangential, and radial stresses  $s'$ ,  $t'$  and  $r'$  in the region  $f$  are removed

$$\left. \begin{aligned} s' &= - \frac{E}{1 - \mu^2} (\lambda + \mu \delta) \\ t' &= - \frac{E}{1 - \mu^2} \cdot \frac{f_b + f}{2f} (\delta + \mu \lambda) \\ r' &= - \frac{E}{1 - \mu^2} \cdot \frac{f_b + f}{2f} (\delta + \mu \lambda) \end{aligned} \right\} . . . . . \quad (17)$$

The whole of the stresses at the region  $f$  are not fully removed by boring out to  $f$ , but if the layer  $df$  at  $f$  is removed the remaining elements of stress  $s''$ ,  $t''$ , and  $r''$  vanish. These are found from the equilibrium conditions from  $ds_b$  and  $dt_b$ —

$$\left. \begin{aligned} s'' &= \frac{E}{1 - \mu^2} (f_b - f) \frac{d(\lambda + \mu \delta)}{df} \\ t'' &= \frac{E}{1 - \mu^2} (f_b - f) \frac{d(\delta + \mu \lambda)}{df} \\ r'' &= 0 \end{aligned} \right\} . . . . . \quad (18)$$

and with

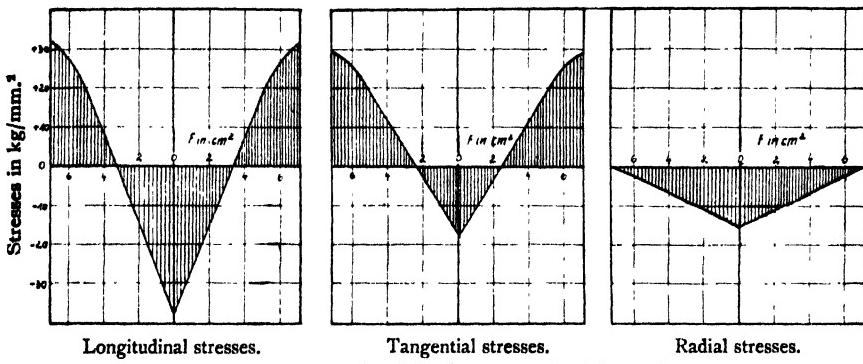
$$E' = \frac{E}{1 - \mu^2}, \quad \Lambda = \lambda + \mu \delta \text{ and } \theta = \delta + \mu \lambda . . . . . \quad (19)$$

we get finally the complete stresses  $s$ ,  $t$ ,  $r$ —

$$\left. \begin{aligned} s &= E' \left[ (f_b - f) \frac{d\Lambda}{df} - \Lambda \right] \\ t &= E' \left[ (f_b - f) \frac{d\theta}{df} - \frac{f_b + f}{2f} \cdot \theta \right] \\ r &= E' \cdot \frac{f_b - f}{2f} \cdot \theta \end{aligned} \right\} . . . . . \quad (20)$$

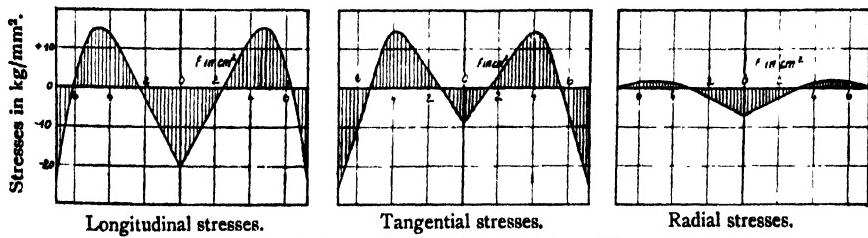
<sup>23</sup> Sachs, *Z. Metallkunde*, 19 (1927), 352.

Measurements on brass rods (58 per cent. Cu) gave in the drawn condition (from 33 mm. to 30 mm.  $\phi$ ) a stress distribution corresponding to Figs. 12 to 14. The longitudinal and tangential stresses at the outer layer lie at 30 kg./mm.<sup>2</sup>, about  $\frac{1}{4}$  of the strength of the material; the internal compressive stresses are in parts even greater. In mercury salt solutions, however, the rod split only after a day as shown in Fig. 15. By straightening the stresses, in the interior, as shown in Figs. 16 to 18, were diminished, and the dangerous tensile stresses in the outer skin were converted into com-



Figs. 12-14.—Internal stresses in a brass (58 per cent.) rod drawn from 33-30 mm.

pression stresses. Nevertheless, a rod segment also split in mercuric chloride solution within a day, although only at the cut surface. By compressing in a machine, somewhat as would occur in practice on hammering, the stresses diminish also, particularly the longitudinal stress. Finally, after heating at 300° the stresses were reduced to, at the most, one twentieth of their original value; the Brinell hardness was only slightly reduced, from 139 to 111. In elongated tensile test pieces of copper and brass no stresses can be observed.



Figs. 16-18.—Internal stresses in a straightened brass rod.

(Communicated later.)—Further to my communication, may I draw attention to the applicability of the maximum load condition to problems of single crystals. The shear stress curve of aluminium crystals depends little upon the orientation.<sup>24</sup> By the aid of the maximum load condition we can estimate with the use of these curves the tensile strength as well as the elongation of any crystal, however orientated.<sup>24</sup> The results are shown in Figs. 19 and 20. A radius vector gives the value of the tensile strength or of the elongation of a crystal of which the direction of the axes of the rod relative to the crystal axis is given by the direction of the radius

<sup>24</sup> Frhr. v. Gölter and Sachs, *Z. techn. Physik*, 8, 586, 1927 (In the press).

vector. The experimental values of the tensile strength of about 20 crystals agree well with calculation, but the experimentally determined values of the elongation prove to be somewhat larger than the calculated values.

## COHESION AT A CRYSTAL SURFACE.

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Although much information of a theoretical nature can be deduced by the methods of thermodynamics and statistical mechanics with regard to surface phenomena, a proper understanding of these phenomena cannot be expected until a detailed knowledge of the forces outside surfaces is available. The object of this paper is to make a first step in this direction by considering the forces outside a surface of a somewhat elementary and idealised character. The point of immediate interest is to find the order of magnitude and the extent of the cohesive forces outside the simple surface considered, for it is hoped that this may indicate the surface forces in other more complicated cases.

The problem of this paper is to investigate the field outside a (100) plane of a crystal of the rocksalt type. The problem is idealised to the extent that the boundary is assumed to be perfectly plane and unlimited in extent. Other boundary planes can equally well be considered<sup>1</sup> (and it is hoped that this will be done in a later paper), but the (100) is known to be the most stable boundary in most heteropolar crystals of the rocksalt type, and it is natural that this should be considered first.<sup>2</sup>

There is a certain simplification introduced by considering crystals of this type, because of the specially simple way in which these crystals are built. It is now generally accepted that the metal atoms give up their valency electrons to the halogen atoms, so that both anions and cations take up a certain known net electrostatic charge. Positive and negative charges may thus be associated with alternate lattice points of the crystal.

In considering the effect of the crystal on a particle outside it we shall make the further assumption that the particle exists alone, unaffected by the presence of other free atoms or ions. We may analyse the cohesion between the outside particle and the crystal under four headings. Firstly, if the particle is charged, there is a direct electrostatic force between the valency charges of the ions in the crystal and the free ion outside it. Secondly, the electronic system of an atom or ion is known to become polarised in the presence of an electric field, so that the electrostatic field of the crystal may be supposed to create an induced dipole at the centre of the atom or ion in its neighbourhood. The reciprocal effect between this dipole and the field producing it gives rise in a non-uniform field to a force of attraction. Thirdly, a free charge outside a crystal polarises the ions in the crystal. Lastly, a force of attraction is known to exist even between

<sup>1</sup> Except the (111) plane, which involves special mathematical difficulties.

<sup>2</sup> The extension of this work to other boundaries may throw some light on the problem of the rate of growth of different crystal planes.

neutral atoms (the van der Waals attraction), and it may be supposed that there is a similar attraction between the electronic systems of ions quite apart from the effect of their valency charges.

The purpose of this paper is to consider in turn these contributions to the total cohesive force between the crystalline solid and an external atom or ion. The mathematical treatment is made as general as possible (except in the case of the polarisation of the crystal itself where special difficulties exist and special investigation is called for), but quantitative determinations are made in only one case and that for purposes of illustration. The case considered is the attraction between an inert gas atom and a crystal of the rocksalt type.

### The Electrostatic Field outside a Crystal.

It is now generally accepted that certain crystals like rocksalt are ionic lattices and that the main cohesive forces between neighbouring particles are simple Coulomb forces between oppositely charged ions. In such crystals there is thus an array of net positive and negative charges, which may be considered to be situated at the lattice points, and the electrostatic potential at any point in space is given by

$$\phi(\mathbf{r}) = \sum_{l, m, n} \frac{e_{l, m, n}}{r_{l, m, n} - r} \quad . . . \quad (2 \cdot 01)$$

where  $e_{l, m, n}$  is the charge at a point  $(l, m, n)$ ,  $r_{l, m, n}$  is the vector defining its position with reference to an arbitrary origin, and  $\mathbf{r}$  is the corresponding vector of the point considered. Owing to the slow convergence of this expression, it is not in general possible to calculate its value by a direct summation, especially when, as in a crystal, the array of charges may be considered as infinite in extent. Special methods have therefore to be devised.

The first consideration of the problem with specific reference to a crystal lattice was made by Madelung<sup>3</sup> in 1918, who gave the potential at any point due first to a row, then to a net-plane and lastly to a space lattice of point charges. A similar method of calculating  $\phi$  was given independently by Ormstein and Zermike,<sup>4</sup> and still later another method was given by Ewald.<sup>5</sup> The applications of these investigations have been in all cases to the calculation of properties inside a crystal, and no application seems to have been made as yet to the field outside a crystal boundary. This is the special problem we consider here.

The method we use is an adaptation of Madelung's method, made by Born<sup>6</sup> and specially applicable to arrays of charges which on the whole are electrically neutral.

In a crystal lattice, the charges are arranged in a regular array with a threefold periodicity, so that the whole crystal can be built up by the adiuxtaposition of a number of identical cells. The unit cell can be specified by three vectors  $a_1, a_2, a_3$ , and the origin of any cell in space is given by

$$\mathbf{r}^i = la_1 + ma_2 + na_3,$$

<sup>3</sup> Madelung, *Physik. Z.*, **19**, 524 (1918). Unknown to Madelung a problem analogous to this had previously been considered by mathematicians without any thought of possible physical applications. Riemann (1880); Appell, *Acta Math.* (4), 313, 1884, etc. Cf. Born, *Atomtheorie des festen Zustandes* (2nd edn.), 1923, p. 715.

<sup>4</sup> Amsterdam Proc., **21**, 911 (1918).

<sup>5</sup> Ewald, *Ann. Physik*, **64**, 253 (1921).

<sup>6</sup> Born, *loc. cit.*

where  $l, m, n$ , are three integers. In each cell there is the same arrangement of charges, and the position of these is determined by the vectors which join them to a point of reference in the cell. If we suppose that there are  $s$  charged particles per cell, we thus have  $s$  vectors  $r_k^l$  ( $k = 1, 2, \dots, s$ ). The position of any charge in space is then determined by a vector

$$\mathbf{r}_k^l = \mathbf{r}_k + \mathbf{r}^l.$$

The summation of (2·01) can then be written

$$\phi(r) = S_l \sum_k \frac{e_k}{|\mathbf{r}_k^l - \mathbf{r}|}$$

where the summation extends over all values of  $k$  and  $l$ .

To illustrate the method of calculating the potential outside a crystal, we consider first a row of charges. In a one-dimensional lattice, the charges are arranged in a line so that after a distance  $a$  the pattern repeats itself. As a preliminary to finding the potential of such a discrete series of charges, the potential of a general distribution of electrical density  $\rho(x)$  can be considered,  $\rho(x)$  being assumed periodic with periodicity  $a$ . The density can then be represented by the usual Fourier expansion as

$$\rho(x) = \sum_{-\infty}^{+\infty} \rho_n e^{\frac{2\pi i n x}{a}} \quad . \quad . \quad . \quad (2 \cdot 011)$$

where  $n$  takes all positive and negative integral values. If the net charge is zero, the constant term in this expansion vanishes. This is indicated in the above equation by adding an accent to the summation sign. The potential at a point outside this electrical system will have the same periodicity in  $x$  as that of  $\rho(x)$  and we can write for the potential at a point  $(x, r)$ , where  $r$  is the radial distance from the line charge,

$$\phi(x, r) = \sum_{-\infty}^{+\infty} f_n(r) e^{\frac{2\pi i n x}{a}} \quad . \quad . \quad . \quad (2 \cdot 012)$$

The potential must satisfy the usual Laplace's equation which in cylindrical co-ordinates with axial symmetry is

$$\frac{\partial^2 \phi}{\partial r^2} + \frac{1}{r} \frac{\partial \phi}{\partial r} + \frac{\partial^2 \phi}{\partial x^2} = 0.$$

When the above expression for  $\phi$  is substituted in this equation the coefficients of each exponential in  $x$  must vanish independently, and we are thus left with a series of differential equations to determine the  $f_n(r)$ . The solution of these is

$$f_n(r) = c_n K_0\left(\frac{2\pi n r}{a}\right),$$

where  $K_0$  is a Hankel function. The arbitrary constant is determined by the condition

$$\rho(x) = -\frac{1}{2} \left[ r \frac{\partial \phi}{\partial r} \right]_{r=0}$$

leading to

$$c_n = 2\rho_n.$$

The solution is thus

$$\phi(x, r) = 2 \sum_{-\infty}^{+\infty} \rho_n K_0\left(\frac{2\pi n r}{a}\right) e^{\frac{2\pi i n x}{a}}.$$

It is easy to pass from the case of continuous distribution  $\rho(x)$  to the series of discrete charges  $e_k$  at points  $x_k$  in the unit cell (with  $\sum_k e_k = 0$ ) and for this case

$$\phi(x, r) = \frac{2}{a} \sum_{-\infty}^{+\infty}' \sum_k e_k K_0\left(\frac{2\pi n r}{a}\right) e^{\frac{2\pi i n (x - x_k)}{a}} . . . (2.02)$$

In the same way, in finding the potential at a point outside a plane lattice Born considers first a continuous distribution of charge doubly periodic with respect to two vectors  $a_1$  and  $a_2$ . In this case the distribution of charge can be represented by a double Fourier expansion. Elegance is gained by the use of the reciprocal vectors  $b_1$  and  $b_2$  where

$$\begin{cases} b_{1x} = \frac{a_{2y}}{|a_1 a_2|}, & b_{1y} = \frac{-a_{2x}}{|a_1 a_2|} \\ b_{2x} = \frac{-a_{1y}}{|a_1 a_2|}, & b_{2y} = \frac{a_{1x}}{|a_1 a_2|} \end{cases} \quad |a_1 a_2| = a_{1x} a_{2y} - a_{2x} a_{1y}$$

In terms of these the distribution of charge can be written

$$\rho = \sum_{l, m}' \rho_{l, m} e^{i(k_{lm} r)},$$

where  $r$  is the vector  $(x, y, 0)$  and

$$k_{lm} = 2\pi(lb_1 + mb_2).$$

The potential must also be doubly periodic in  $a_1$  and  $a_2$  and writing an expression analogous to (2.012) in the one-dimensional case, using Laplace's equation and using the boundary condition

$$\left(\frac{\partial \phi}{\partial z}\right)_{z=0} = -2\pi\rho,$$

the potential is found to be

$$\phi = 2\pi \sum_{l, m}' \frac{\rho_{l, m}}{|k_{l, m}|} \cdot e^{i(k_{l, m} r) - |k_{l, m}| |z|}$$

For an array of point charges  $e_k$  at points  $r_k$   $(x_k, y_k, 0)$ , which is the limiting case of that just considered, we find

$$\phi(x, y, z) = \frac{2\pi}{|a_1 a_2|} \sum_k \sum_{l, m}' e_k \frac{e^{-|k_{l, m}| |z|}}{|k_{l, m}|} e^{i(k_{l, m} r - r_k)} . . . (2.03)$$

We now apply this expression to the detailed consideration of the (100) boundary of a crystal of the NaCl type. (Blut and Stark (*Z. Physik*, 43, 575, 1927) have recently applied the same method independently to find the field outside a NaCl crystal, though not in the same detail as in this paper.) In this case it is convenient to take as unit cell a square of side  $a$  containing 4 charges ( $\pm ve$  where  $v$  is the valency) situated according to the following scheme (see p. 96).

The vector  $a_1$  is in the direction of  $x$ , and  $a_2$  in the direction of  $y$  with  $|a_1| = |a_2| = a$ , and so  $b_1$  is in the direction of  $x$ ,  $b_2$  in the direction of  $y$  and  $|b_1| = |b_2| = \frac{1}{a}$ .

Hence

$$k_{l, m} = 2\pi\left(\frac{l}{a} + \frac{m}{a}\right)$$

$k$	$e_k$	$r_k$	$r - r_k$	$(k_l, m, r - r_k)$
1	$+ve$	(0, 0, 0)	( $x, y, z$ )	$\frac{2\pi}{a}(lx + my)$
2	$-ve$	$\left(\frac{a}{2}, 0, 0\right)$	$\left(x - \frac{a}{2}, y, z\right)$	$\frac{2\pi}{a}\left(lx - \frac{a}{2} + my\right)$
3	$-ve$	$\left(0, \frac{a}{2}, 0\right)$	$\left(x, y - \frac{a}{2}, z\right)$	$\frac{2\pi}{a}\left(lx + my - \frac{a}{2}\right)$
4	$+ve$	$\left(\frac{a}{2}, \frac{a}{2}, 0\right)$	$\left(x - \frac{a}{2}, y - \frac{a}{2}, z\right)$	$\frac{2\pi}{a}\left(lx - \frac{a}{2} + my - \frac{a}{2}\right)$

and the real part of the potential is

$$\phi(x, y, z) = \frac{2\pi}{a^2} \sum'_{l, m} \frac{e^{-\frac{2\pi}{a}\sqrt{l^2+m^2}z}}{\frac{2\pi}{a^2}\sqrt{l^2+m^2}} \sum_k e_k \cos(k_l, m, r - r_k), \quad (2.04)$$

The summation over the charges  $e_k$  gives

$$\begin{aligned} ve \left\{ \cos \frac{2\pi}{a}(lx + my) - \cos \frac{2\pi}{a}\left(lx - \frac{a}{2} + my\right) - \cos \frac{2\pi}{a}\left(lx + my - \frac{a}{2}\right) \right. \\ \left. + \cos \frac{2\pi}{a}\left(lx - \frac{a}{2} + my - \frac{a}{2}\right) \right\} \\ = -4ve \left\{ \cos 2\pi\left(\frac{lx}{a} + \frac{my}{a} - \frac{l+m}{4}\right) \sin \frac{\pi l}{2} \sin \frac{\pi m}{2} \right\} \dots \dots \dots \quad (2.05) \end{aligned}$$

Since  $\sin \frac{s\pi}{2} = 0$  when  $s$  is even, it follows that the summation in (2.04) above need be taken over odd values of  $l$  and  $m$  only and for such values  $\sin \frac{\pi l}{2} \sin \frac{\pi m}{2} = (-1)^{\frac{l+m-2}{2}}$ . Hence

$$\phi(x, y, z) = \frac{4ve}{a} \sum'_{l, m} (-1)^{\frac{l+m-2}{2}} \frac{e^{-\frac{2\pi z}{a}\sqrt{l^2+m^2}}}{\sqrt{l^2+m^2}} \cos 2\pi\left(\frac{lx}{a} + \frac{my}{a} - \frac{l+m}{4}\right) \quad (2.06)$$

This gives the potential due to the surface layer only. That of the layer just below the surface plane is found by substituting  $z + \frac{a}{2}$  for  $z$  everywhere and changing the signs of the charges. Similarly, the potential of successive lower layers is obtained by adding successive increments of  $\frac{a}{2}$  to  $z$ . These form a geometrical progression, so that the potential of the whole crystal bounded by a (100) plane at a point outside it is easily seen to be

$$\phi = \frac{4ve}{a} \sum'_{l, m} \frac{(-1)^{\frac{l+m-2}{2}}}{\sqrt{l^2+m^2}} \cos 2\pi\left(\frac{lx}{a} + \frac{my}{a} - \frac{l+m}{4}\right) \frac{e^{-\frac{2\pi z}{a}\sqrt{l^2+m^2}}}{1+e^{-\pi\sqrt{l^2+m^2}}} \quad (2.07)$$

The force on a unit charge at  $(x, y, z)$  is, of course, given by  $-\text{grad } \phi$ , but it is the component normal to the surface which is of greatest interest, and this is given by

$$F_z = -\frac{\partial \phi}{\partial z} = \frac{8\pi ve}{a^2} \sum'_{l, m} \frac{(-1)^{\frac{l+m-2}{2}}}{1+e^{-\pi\sqrt{l^2+m^2}}} e^{-\frac{2\pi z}{a}\sqrt{l^2+m^2}} \cos 2\pi\left(\frac{lx}{a} + \frac{my}{a} - \frac{l+m}{4}\right) \quad (2.08)$$

The first permissible values of  $l$  and  $m$  are  $(\pm 1, \pm 1)$ , the second are  $(\pm 1, \pm 3)$  and  $(\pm 3, \pm 1) \dots$ . The first term in the series is by far the most important; for instance, when  $x = y = 0$ , the ratio of the second term to the first is less than 1 per cent. To give an idea of the variation of  $F_z$  over the surface of the crystal it is thus sufficient as a first approximation to consider only the group of terms in the expansion for which  $l^2 + m^2 = 2$ . Writing

$$F_1 = \frac{8\pi ve}{a^2} \frac{e^{-2\sqrt{2\pi z}/a}}{1 + e^{-\sqrt{2\pi}}} \dots \quad (2.09)$$

we then find that

$$F_z = \rho F_1 \dots \quad (2.10)$$

where  $\rho$  depends only on the co-ordinates  $x$  and  $y$ . The variation of  $\rho$  over a unit cell is indicated by the following Table.

TABLE I.—VARIATION OF NORMAL ELECTROSTATIC FORCE OVER A PLANE PARALLEL TO THE SURFACE.

$\frac{y}{a}$	0.	$\frac{1}{2}$ .	$\frac{1}{4}$ .	$\frac{3}{4}$ .	$\frac{1}{2}$ .
0	$4$	$2\sqrt{2}$	$2\sqrt{2}$	0	$-2\sqrt{2}$
$\frac{1}{2}$	$2\sqrt{2}$	0	0	0	$-2\sqrt{2}$
$\frac{1}{4}$	0	0	0	0	0
$\frac{3}{4}$	$-2\sqrt{2}$	$-2$	$-2$	$2$	$2\sqrt{2}$
$\frac{1}{2}$	$-4$	$-2\sqrt{2}$	0	$2\sqrt{2}$	4

The force is a maximum, for any given value of  $z$ , above the lattice points of the crystal and is zero at all points of those planes normal to the surface which bisect the lines joining adjacent ions.

It is the variation of the force with distance from the surface which is of greatest interest. This we calculate in detail for a series of points above the lattice points. We have, from (2.08),

$$F_z = \frac{8\pi ve}{a^2} \sum'_{l,m} c_{l,m} f_{l,m}(z) \dots \quad (2.11)$$

$$\text{where } c_{l,m} = \frac{(-1)^{\frac{l+m}{2}} \cos \left( \frac{l+m}{2} \right) \pi}{1 + e^{-\pi \sqrt{l^2 + m^2}}} \dots \quad (2.12)$$

$$\text{and } f_{l,m}(z) = e^{-2\pi z/a\sqrt{l^2 + m^2}} \dots \quad (2.121)$$

The first four values of  $c_{l,m}$  are given in Table II. The first column gives

TABLE II.—VALUES OF  $c_{l,m}$ .

$l^2 + m^2$	$\frac{m}{(-1)^{\frac{l+m}{2}} \cos \frac{(l+m)\pi}{2}}$	$1 + e^{-\pi \sqrt{l^2 + m^2}}$	$c_{l,m}$
2	4	1.0118	3.953
10	8	1.0000	8.000
18	4	1.0000	4.000
26	8	1.0000	8.000

a series of permissible values of  $l^2 + m^2$  for  $l$  and  $m$  both odd. The corresponding values of the functions  $c_{l,m} f_{l,m}(z)$  for several values of  $z$  are given in Table III.

TABLE III.—VALUES OF  $c_{l,m} f_{l,m}(z)$  AND  $eF_z$  (THE FORCE ON  $a + e$  CHARGE).

$z/a =$	0.5.	0.6.	0.7.	0.8.	0.9.	1.0.	1.5.
$\frac{p+m^2}{2} c_{l,m} f_{l,m}(z)$	$4.650 \cdot 10^{-2}$	$1.912 \cdot 10^{-2}$	$7.864 \cdot 10^{-3}$	$3.234 \cdot 10^{-3}$	$1.330 \cdot 10^{-3}$	$5.470 \cdot 10^{-4}$	$6.433 \cdot 10^{-4}$
10	"	0.039	0.005	0.007	0.001	0.000	0.000
18	"	0.001	0.000	0.000	0.000	0.000	0.000
26	"	0.000	0.000	0.000	0.000	0.000	0.000
$\Sigma c_{l,m} f_{l,m}(z)$	$4.690 \cdot 10^{-2}$	$1.918 \cdot 10^{-2}$	$7.871 \cdot 10^{-3}$	$3.235 \cdot 10^{-3}$	$1.330 \cdot 10^{-3}$	$5.470 \cdot 10^{-4}$	$6.433 \cdot 10^{-4}$
$eF_z$	$8.46 \cdot 10^{-5}$	$3.46 \cdot 10^{-5}$	$1.42 \cdot 10^{-5}$	$5.84 \cdot 10^{-6}$	$2.40 \cdot 10^{-6}$	$9.87 \cdot 10^{-7}$	$1.16 \cdot 10^{-6}$

This table shows how rapidly the series converges and how close an approximation is given by the first term alone.

In order to give some idea of the magnitude of the force at various distances, a particular case is considered, viz., NaCl in which  $v = 1$  and the distance between neighbouring atoms is  $2.815\text{\AA}$  so that  $a = 5.63\text{\AA}$ . The last row in the above table gives the force in dynes for this value of  $a$ . The electrostatic force outside the (100) plane of other similar crystals can be deduced by multiplying the last row by the constant ratio  $v_2 a_1^2 / a_2^2$ , where  $v_2$  is the valency of the charges in the second crystal, and  $a_1/a_2$  is the ratio of the sides of unit cells.

It is interesting to observe that the force is reduced by  $1/100$  by increasing  $z/a$  from 0.5 to 1 (*i.e.*, increasing  $z$  from  $2.815$  to  $5.63\text{\AA}$  in the case of NaCl).

The work required to separate a charge  $e$  from a point at a distance  $z$  away from the surface is clearly  $e\phi(z)$ . For a fixed value of  $z$ , this is the same function of  $x$  and  $y$  as  $F_z$  already considered and is indicated in Table I. It is obviously a maximum for points above the lattice points of the surface. For such points

$$e\phi(z) = \frac{4e^2}{a} \sum_{l,m} \frac{c_{l,m}}{\sqrt{l^2 + m^2}} f_{l,m}(z). \quad . \quad . \quad (2.13)$$

in the notation of (2.12) and (2.121).

A series of values of  $c_{l,m}$  and  $f_{l,m}(z)$  have already been given in Tables II. and III. and so the corresponding values of  $e\phi(z)$  can easily be deduced. As an example, the values have been worked out for NaCl as before (assuming  $a = 5.63\text{\AA}$ ) and are given in Table IV.

TABLE IV.—THE WORK REQUIRED TO SEPARATE A CHARGE  $e$  FROM THE CRYSTAL.

$\frac{z}{a}$	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{4}$	$\frac{1}{5}$	$\frac{1}{6}$	$\frac{1}{7}$	$\frac{1}{8}$
$e\phi(z) \cdot 10^{18} \text{ ergs.}$	5.36	2.45	1.23	0.64	0.28	0.14	0.06

The work required to separate a permanent dipole of length  $l$  from the crystal against the electrostatic field is clearly  $e[\phi(z) - \phi(z + l)]$ . If  $l$  is large, Table IV. shows that  $\phi(z + l) < \phi(z)$ , so that the work required is approximately  $e\phi(z)$ . This gives the order of magnitude of the work required to separate a molecule of known permanent electric moment from the crystal surface against the electrostatic field. It is seen to be about  $5 \cdot 10^{-13}$  ergs. if  $z$  is about  $3\text{\AA}$ . This corresponds to a heat of adsorption of the order of 7000 calories per gram molecule (neglecting the influence of the molecules on each other).

It may be of interest to observe that if a number of long dipoles were arranged on the crystal surface opposite each lattice point and oriented alternately in one direction and then the other, the electrostatic field outside the projecting ends of the dipoles would be approximately the same as that of the crystal itself, however long the dipole. (This is, because the first layer of the crystal has by far the most important effect, cf. equations (2.06) and (2.07)). It would then be easy for another such layer of dipoles to form on top of the first and so on indefinitely. This may be relevant with regard to some phenomena of adhesion recently observed.<sup>7</sup>

### The Polarisation of a Neutral Atom in the Electrostatic Field of a Crystal.

The above calculations give the electrostatic force outside a crystal and therefore give the forces on a charged ion approaching the crystal surface. When a neutral atom approaches, there is no electrostatic attraction but there is an induced attraction which we now consider. In the theory of dielectrics and elsewhere, it is assumed that an atom is polarised in an electric field, the strength of the induced dipole being proportional to the applied field. Strictly this assumption is only valid for a weak homogeneous field, but as a first approximation we may suppose that an atom is polarised according to the same law in a field outside a crystal. The moment of the induced dipole is then  $p = aF$ , where  $a$  is an atomic constant, called the coefficient of polarisability. The potential energy of the dipole in the electric field  $F$  is  $pF = aF^2$ . On the other hand the dipole has a certain quasi-elastic energy  $(\frac{1}{2})aF^2$ . The net potential energy of the dipole in the field is the difference of these two and is therefore  $\frac{1}{2}aF^2$ . In terms of the electrostatic potential given above, equation (2.07), we have for the potential energy of the dipole,

$$\Phi = \frac{1}{2}a \left\{ \left( \frac{\partial \phi}{\partial x} \right)^2 + \left( \frac{\partial \phi}{\partial y} \right)^2 + \left( \frac{\partial \phi}{\partial z} \right)^2 \right\} \quad . \quad . \quad (3.01)$$

The force on the dipole is then given by

$$\mathbf{F} = - \operatorname{grad} \Phi.$$

The component of force perpendicular to the crystal surface is

$$F_z = - \frac{\partial \Phi}{\partial z} = - a \left\{ \frac{\partial \phi}{\partial x} \cdot \frac{\partial^2 \phi}{\partial x \partial z} + \frac{\partial \phi}{\partial y} \cdot \frac{\partial^2 \phi}{\partial y \partial z} + \frac{\partial \phi}{\partial z} \cdot \frac{\partial^2 \phi}{\partial z^2} \right\}.$$

In order to find the variation of this force over a plane parallel to the crystal surface and at a distance  $z$  from it, we may use in this expression the

<sup>7</sup> Hardy and Nottage, *Proc. Roy. Soc.*, **112**, 62 (1926), McBain and Lee, *Proc. Roy. Soc.*, **113**, 606 (1927).

values of  $\phi$  obtained from (2.07) by taking only the part given by  $(l, m) = (\pm 1, \pm 1)$ . We then obtain after some reduction,

$$\text{where } \mathfrak{F}_0 = + \frac{2(32)^2 \cdot \sqrt{2 \cdot \pi^3 v^2 e^2 a}}{a^5} \cdot \frac{e^{-4\sqrt{2\pi z/a}}}{(1 + e^{-\sqrt{2\pi z/a}})^2}$$

and is the force opposite a lattice point, while  $f$  is a pure number given by

$$f = \frac{1}{2} \left\{ 1 - \cos 2\pi \left( \frac{x}{a} + \frac{y}{a} - \frac{1}{2} \right) \cos 2\pi \left( \frac{x}{a} - \frac{y}{a} \right) \right\}.$$

A few values of  $f$  are given in Table V. to give a rough idea of the variation of  $\mathfrak{F}_0$  with  $x$  and  $y$ . Like  $F_z$ , it is a maximum opposite the lattice points.

TABLE V.—VALUES OF  $f$ .

$y/a$	$x/a$	$a$	$1/4$	$1/2$
0	0	1	1	1
$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	0	$\frac{1}{2}$
$\frac{1}{2}$	$\frac{1}{2}$	1	$\frac{1}{2}$	1
$\frac{3}{4}$	$\frac{3}{4}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$

The accurate expression for  $\mathfrak{F}_0$  is

$$\mathfrak{F}_0 = \frac{128a\pi^3 e^2}{a^5} \cdot \sum'_{l, m} c_{l, m} f_{l, m}(z) \sum'_{l, m} \sqrt{l^2 + m^2} c_{l, m} f_{l, m}(z)$$

in the notation of (2.12) and (2.121). A particular case will bring out the order of magnitude of this force. We consider Argon (for which  $a = 1.63 \cdot 10^{-10}$ )<sup>8</sup> near the surface of NaCl (for which  $a = 5.63 \text{ \AA}$ ). The values of  $\mathfrak{F}_0$  for a series of values of  $z/a$  are given in Table VI.

TABLE VI.

$z/a$	0.5.	0.6.	0.7.	0.8.	0.9.	1.0.	1.5.
$\mathfrak{F}_0$	$8.19 \cdot 10^{-6}$	$1.36 \cdot 10^{-6}$	$2.29 \cdot 10^{-7}$	$3.86 \cdot 10^{-8}$	$6.52 \cdot 10^{-9}$	$1.10 \cdot 10^{-9}$	$1.53 \cdot 10^{-13}$

The force is naturally very much less than the electrostatic force  $F_z$ , and falls away much more rapidly. When  $z$  is increased from  $a/2$  ( $2.81 \text{ \AA}$ ), to  $a$ , ( $5.63 \text{ \AA}$ ),  $\mathfrak{F}_0$  is decreased by  $10^{-4}$ .

### Van der Waals' Cohesive Forces.

Although the existence of cohesive forces between atoms, even when uncharged, has long been recognised, there is still very little accurate information as to the nature or magnitude of these forces. Two methods only seem to have been tried. One of these uses observations of the viscosity of gases<sup>9</sup> and the other the observed isothermals of gases.<sup>10</sup> The

<sup>8</sup> Born and Heisenberg, *Z. Physik.*, **23**, 396, 1924.

<sup>9</sup> Chapman, *Phil. Trans.*, **A. 216**, 279 (1915); James, *Proc. Camb. Phil. Soc.* **20**, 447 (1921); Lennard-Jones, *Proc. Roy. Soc.*, **A. 106**, 441 (1924); Hassé and Cook, *Phil. Mag.*, **3**, 977 (1927).

<sup>10</sup> Keesom, *Comm. Phys. Lab. Leiden. Suppl.*, No. 24 (1912) or *Proc. Sect. Sci. Amst. rdam*, **15**, (1), 256; Zwicky, *Physik. Z.*, **22**, 449 (1921); Lennard-Jones, *Proc. Roy. Soc.*, **A. 106**, 463 (1924); Lennard-Jones and Cook, *Proc. Roy. Soc. A.* **112**, 214 (1926).

former cannot be said to have yielded reliable information at present, because, with one exception, the theoretical formulæ which are used postulate a weaker attractive field than is known to exist. The exceptional case is that considered recently by Hassé and Cook,<sup>9</sup> in which the molecular model is a rigid sphere surrounded by an attracting field varying as the inverse fifth power of the distance and of any magnitude. For mathematical reasons the restriction to this particular type of attracting force is necessary. The method requires observations of the viscosity of a gas extending over a wide range of temperature and only in a few cases is sufficient data available.

The second method is more satisfactory from the mathematical point of view, because it permits of greater flexibility in the molecular models chosen. Thus it is possible to consider a repulsive field varying as one inverse power of the distance, together with an attractive field varying as another ( $\lambda r^{-n} - \mu r^{-m}$ ). The method shows what pairs of values of  $n$  and  $m$  are suitable and for these determines the numerical magnitudes of  $\lambda$  and  $\mu$ .

Up to now greatest importance has been attached to the repulsive force constant  $\lambda$  and its appropriate index  $n$ , but the quantitative results which have been obtained with regard to  $\mu$  and  $m$  can now be applied to the problem here considered. Without entering into great detail, it may be said that for most gases  $m = 5$  has proved to be most satisfactory, though values  $m = 6$  and  $m = 7$  are not definitely ruled out. It is unlikely that  $m$  is greater than 7, because the index of the repulsive field is of the order 10 (9, 10, or 11) and the physical properties of gases demand that the repulsive field shall fall away more quickly than the attractive field.

Quantitative determinations of these Van der Waals' attractive fields can only be made for the atoms of a gas, that is for neutral atoms. The origin of the forces is not definitely known, but it is surmised that each atom is polarised in the presence of others and the temporary distortion of the electronic shells gives rise to an attraction. It is to be expected therefore that similar forces will exist between the electronic cores of ions in addition to the electrostatic forces already considered. While there is no quantitative information about such forces between ions, it may be supposed that they are of the same type and of the same order of magnitude as those between neutral atoms, particularly when, as in NaCl, the electronic shells of the ions are of the inert gas type. In order to make a rough estimate of the van der Waals' attraction between an inert gas atom (an argon atom, say) and the NaCl crystal, we may suppose all the ions in the crystal to have argon-like cores, though actually the Na ions have neon-like cores.

Consider an atom at a distance  $z$  from the (100) plane boundary of a NaCl crystal and opposite a lattice point, which for convenience we may regard as the origin. Since the co-ordinates of any lattice point of the crystal can be written as  $la/2$ ,  $ma/2$ ,  $na/2$  in the previous notation,  $l$ ,  $m$ ,  $n$  being any integers positive or negative, while  $n$  takes positive integral values only, the force between the atom outside the crystal and one of the ions inside is given by

$$\mu(2/a)^s \left\{ l^2 + m^2 + \left( \frac{2z}{a} + n \right)^2 \right\}^{-s/2} \quad . \quad . \quad . \quad (4.01)$$

if the force varies as the inverse  $s$ th power of the distance ( $\mu r^{-s}$ ). The total force due to the whole crystal resolved perpendicular to the surface is thus seen to be

$$H = \mu(2/a)^s \cdot H^{(s)}(z) \quad . \quad . \quad . \quad . \quad (4.02)$$

where

$$h^{(s)}(z) = \sum_{l, m, n} \left( \frac{2z}{a} + n \right) \left\{ l^2 + m^2 + \left( \frac{2z}{a} + n \right)^2 \right\}^{-(s+1)/2} \quad (4.021)$$

and the summation extends over all values of  $l$ ,  $m$ , and  $n$  while  $h^s(z)$  is a function of  $z$  only. No general method has yet been given for the summation of such a series, and, as it is found to converge very slowly for the values  $s = 5$  and  $s = 6$ , the following method has been used.

The effect of all the atoms within a distance  $z + c$  of the outside atom has been calculated by a direct summation. This part is denoted by  $H_1$ . Outside this spherical cap, the crystal is regarded as a continuum over which the force centres are distributed uniformly. Let this part be  $H_2$ . Its value is easily calculated as follows:—

Let the attraction of a volume element  $v$  be  $(\rho \cdot dv)r^{-s}$ , so that the potential of a thin spherical cap of radius  $\xi$  and thickness  $d\xi$ , terminated by the boundary of the crystal ( $z = 0$ ) is

$$d\phi = \frac{\rho 2\pi \xi (\xi - z) d\xi}{(s-1)\xi^{s-1}} \quad . \quad . \quad . \quad (4.03)$$

Since one force constant  $\mu$  is associated with each element of volume  $a^3/8$ , we have  $\rho = 8\mu/a^3$ . Using this value and integrating the above expression throughout the range of  $\xi$ , which is  $z + c$  to infinity, we find

$$\phi = \frac{16\pi\mu}{a^3} \cdot \frac{z + (s-3)c}{(s-1)(s-3)(s-4)(z+c)^{s-3}} \quad . \quad . \quad . \quad (4.04)$$

We deduce that

$$H_2 = - \frac{16\pi\mu}{a^3} \cdot \frac{z + (s-2)c}{(s-1)(s-3)(z+c)^{s-2}} \quad . \quad . \quad . \quad (4.05)$$

For the particular case of  $s = 5$ , we have

$$\phi = \frac{2\pi\mu}{a^3} \cdot \frac{z + 2c}{(z+c)^5}; \quad H_2 = - \frac{2\pi\mu}{a^3} \cdot \frac{z + 3c}{(z+c)^3} \quad . \quad . \quad . \quad (4.06)$$

It is interesting to note in passing that these expressions tend asymptotically to

$$\phi = \frac{2\pi\mu}{a^3 z}; \quad H_2 = - \frac{2\pi\mu}{a^3 z^2} \quad . \quad . \quad . \quad (4.07)$$

so that at a large distance the force falls off as the inverse square of the distance. The van der Waals' field, usually regarded as a short range force here becomes one of long range.

Corresponding to the two contributions  $H_1$  and  $H_2$  to  $H$ , it is convenient to write

$$h^{(s)}(z) = h_1^{(s)}(z) + h_2^{(s)}(z),$$

where

$$h_2^{(s)}(z) = H_2 \div \mu(z/a)^s = \frac{1}{(s-1)(s-3)} \cdot \frac{2\pi(z' + s-2c')}{(z' + c')^{s-2}},$$

$z'$  being written for  $2z/a$  and  $c'$  for  $2c/a$ .

Their values for  $s = 5$  and  $s = 6$  are given for a series of values of  $z/a$  in Table VII.

TABLE VII.

$z/a$ .	0·5.	0·7.	1·0.	1·5.
No. of atoms in spherical cap.	$3a/2$ 104	$3a/2$ 124	$3a/2$ 148	$3a/2$ 196
$h_1^{(5)}(z)$	1·96	0·70	0·26	0·08
$h_2^{(5)}(z)$	0·12	0·10	0·07	0·04
$h^{(5)}(z)$	2·08	0·80	0·33	0·12
$h_1^{(6)}(z)$	1·562	0·376	0·096	0·021
$h_2^{(6)}(z)$	0·021	0·015	0·009	0·005
$h^{(6)}(z)$	1·583	0·391	0·105	0·026
H in dynes ( $m = 5$ )	$1\cdot92 \cdot 10^{-5}$	$7\cdot39 \cdot 10^{-6}$	$3\cdot02 \cdot 10^{-6}$	$1\cdot16 \cdot 10^{-6}$
H in dynes ( $m = 6$ )	$5\cdot47 \cdot 10^{-5}$	$1\cdot35 \cdot 10^{-5}$	$3\cdot62 \cdot 10^{-6}$	$8\cdot83 \cdot 10^{-7}$

To test the accuracy of this method of approximating to the value of  $h(z)$ , the values of  $h_1^{(5)}(z)$  and  $h_2^{(5)}(z)$  for  $z/a = 0\cdot5$  were calculated for another value of  $c$ , viz.,  $c = a$ . The results are  $h_1^{(5)}(z) = 1\cdot897$ ,  $h_2^{(5)}(z) = 0\cdot204$  giving  $h^{(5)}(z) = 2\cdot10$ . As this calculation only involves the direct summation of 47 atoms compared with 104 when  $c = 3a/2$ , the proximity of this result to that given in the table lends support to the method of approximation.

The numerical values of H for  $\mu = 1\cdot63 \cdot 10^{-43}$  appropriate to two argon atoms<sup>11</sup> and  $a = 5\cdot63 \text{\AA}$  appropriate to NaCl are included in Table VII.

As the value of  $m$  is somewhat uncertain, it has been thought of interest to work out the attractive field for  $m = 6$  as well, particularly as the appropriate force constant for Argon atoms has also been evaluated.<sup>12</sup> The calculations are summarised in Table VII. It is interesting to observe that the two fields thus calculated have approximately the same values from  $z = a$  to  $z = 3a/2$  in this particular case.

### The Polarisation of a Crystal by a Charge outside it.

There remains one further effect to be considered and that is the polarisation of the ions in the crystal by a charged particle outside it. This has purposely been postponed because its consideration involves special difficulties. Up to now we have investigated the problem of the interaction of a crystal and an atom or ion outside it, making the tacit assumption that the latter is isolated from all others. We have supposed the crystal structure to be known and definite and to be unaffected by the presence of the external body. This is probably a sufficiently accurate representation of the facts when the outside particle is uncharged, but complications occur when it has an electrostatic charge. In the first place it polarises the ions of the crystal. The induced dipoles may be supposed in each case to be proportional to the field and then, by an argument similar to that used in § 3, we may show that an attraction is set up between the induced dipole and the charge producing it, equal to  $2ae^2/r^6$ ,

<sup>11</sup> Lennard-Jones and Cook, *Proc. Roy. Soc., A.*, 112, 214, § 4 (1926).

<sup>12</sup> Lennard-Jones and Taylor, *Proc. Roy. Soc., A.*, 109, 476, Table XXIV. (1925).†

where  $\alpha$  is the coefficient of polarisability of the ion and  $\epsilon$  is the magnitude of the outside charge.<sup>13</sup> This attraction is of the same type as that considered in the last paragraph and can be summed over the crystal by the same method. If we take  $\alpha$  to be the same for both ions,<sup>14</sup> the total force on the outside ion normal to the crystal face due to the polarisation of the crystal is  $2\alpha e^2(2/\alpha)^5 \cdot h^{(5)}(z)$ , the numerical value of which can easily be computed in any given case for any value of  $z$  by using the values of  $h^{(5)}(z)$  given in Table VII.

There is, however, a second factor to be taken into account. A charged ion would never in actual practice be sufficiently isolated for the calculations in the preceding paragraph to be valid. As shown in Debye's theory of electrolytes, a charged ion would carry about with it an atmosphere of other ions of opposite sign, and these would tend to neutralise the polarisation of the crystal caused by the ion itself. The effect of this atmosphere, if of the same type as that of Debye's, could again be calculated, but this will itself be modified by the presence of the crystal. The problem cannot therefore be considered as a statical one, but must be regarded as an example of statistical mechanics. The distribution of the ions depends on the potential field outside the crystal, and this again depends on the distribution. One result, however, may be inferred from considerations of symmetry, and that is that the polarising field at each ion in the surface of the crystal will be normal to the surface and will be directed alternately into and out of the crystal at the lattice points. Above a positive ion, for instance, negative ions are likely to predominate and thus to determine the direction of the induced dipole. On the other hand this surface ion will be polarised in the opposite direction by the unbalanced electrostatic field of the ions in the interior of the crystal, so that the net polarisation of the surface ions is likely to be small. A quantitative treatment of this problem must be deferred for the present.

### Discussion of the Results.

The various numerical results obtained in the paper for particular cases are illustrated in the Figure. It is unsafe to draw general conclusions from the results for special cases, but it is hoped that the curves do illustrate the laws of force outside crystals of the rock salt type. For instance, the electrostatic field outside the (100) plane of crystals other than rock salt, but of the same type, can be deduced from that shown by altering all the ordinates in a fixed ratio. The curve does indicate therefore the rapid way in which the electrostatic field falls off outside such crystals.

The van der Waals' field, on the other hand, falls off according to an inverse second or third power of the distance and so becomes of greater importance than the electrostatic field at long distances. In this respect, the electrostatic forces and the van der Waals' force change their usual rôles, for it is the former which are usually regarded as long range forces, and the latter as the short range forces. The results would suggest that the van der Waals' forces act as the first agents in the process of adsorption of atoms or ions and that the electrostatic forces serve to clinch the capture and ultimate adsorption.

This result emphasises the need for a more extensive and detailed investigation of van der Waals' cohesive forces. A method of determining them

<sup>13</sup> Cf. Born and Heisenberg, *Z. Physik.*, **23**, 337 (1924).

<sup>14</sup> Actually the polarisabilities of the ions in a crystal like NaCl are different. This could easily be taken into account if necessary by making a suitable modification in the method of the previous paragraph.

for gaseous atoms and molecules has recently been given<sup>15</sup> and awaits only more extensive experimental material. It is hoped that this will soon be forthcoming.

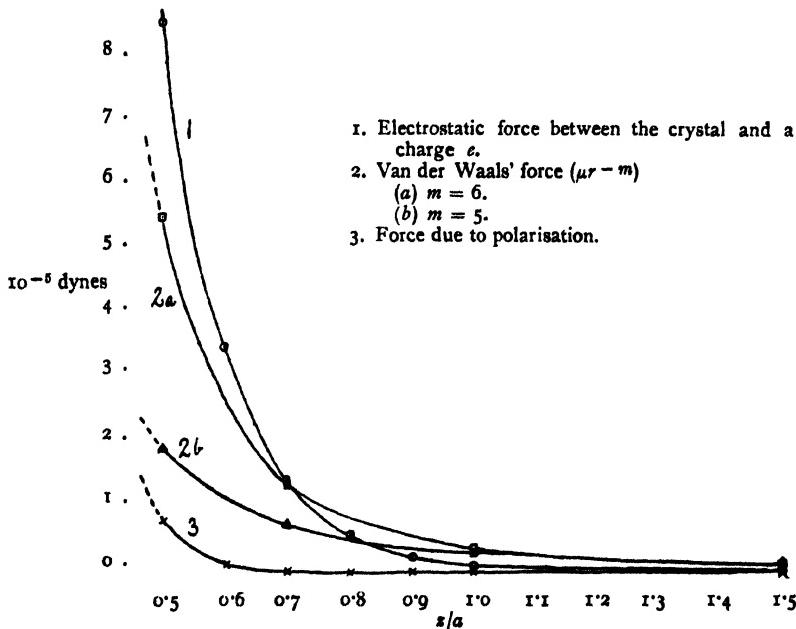


FIG. 1.—Cohesive forces outside a crystal surface.

**Appendix (added in proof).**—The above work has since been supplemented by the calculation of the potential field outside the crystal. The potential of a singly charged ion in the electrostatic field of the crystal  $\phi^{(e)}$  has already been considered and is given by  $e\phi(z)$  where  $\phi(z)$  is defined in equation (2.07). Numerical values of this quantity appropriate to NaCl are given in Table IV., and the corresponding quantities for other crystals of the same type can be obtained by multiplying by a factor  $a'/a$ , where  $a'/_2$  is the shortest distance between ions in the crystal.

The potential of a neutral atom due to polarisation by the crystal  $\phi^{(p)}$  is  $\frac{1}{2}aE^2$ , or, opposite a lattice point,  $\frac{1}{2}aF_s^2$ .  $eF_s$  has been given for NaCl in Table III., so that the contribution to the potential is easily evaluated. The results of the calculation are

$z/a =$	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5
$\phi^{(p)}(z)$	$2.56 \cdot 10^{-14}$	$4.27 \cdot 10^{-15}$	$7.20 \cdot 10^{-16}$	$1.22 \cdot 10^{-16}$	$2.06 \cdot 10^{-17}$	$3.48 \cdot 10^{-18}$	$4.80 \cdot 10^{-19}$				

The contribution of the van der Waals' forces to the potential  $\phi^{(w)}$  is

$$\frac{\mu}{s-1} \left(\frac{2}{a}\right)^{s-1} \sum_{l,m,n} \left\{ l^2 + m^2 + \left(\frac{2z}{a} + n\right)^2 \right\}^{-(s-1)/2}.$$

This summation can be evaluated like  $k^s(z)$  in equation (4.021), viz., by dividing the crystal into two parts by a spherical cap and considering

<sup>15</sup> Cf. Lennard-Jones and Cook, Proc. Roy. Soc., A, 115, 334 (1927).

separately those ions within and those without the cap. Corresponding to these two parts we have

$$\phi^{(w)}(z) = \frac{\mu}{(s-1)} \left(\frac{2}{a}\right)^{s-1} \{ f_1^{(s)}(z) + f_2^{(s)}(z) \}$$

and the numerical values of  $f_1^{(s)}(z)$  and  $f_2^{(s)}(z)$  for crystals of the NaCl type are given in Table VIII. (These have been tested by taking spherical caps of different heights, as explained in the paper above.) The values for

TABLE VIII.

s.	$z/a =$	0.5.	0.7.	1.0.	1.5.
5	$f_1^{(s)}(z)$	3.764	1.942	0.960	0.420
5	$f_2^{(s)}(z)$	1.374	1.201	1.005	0.785
5	$f_1^{(s)}(z) + f_2^{(s)}(z)$	5.138	3.143	1.965	1.205
	$\phi^{(w)}(z)$	$3.34 \cdot 10^{-13}$	$2.05 \cdot 10^{-13}$	$1.28 \cdot 10^{-13}$	$7.83 \cdot 10^{-14}$
6	$f_1^{(s)}(z)$	2.460	0.900	0.323	0.0997
6	$f_2^{(s)}(z)$	0.114	0.091	0.067	0.0437
6	$f_1^{(s)}(z) + f_2^{(s)}(z)$	2.574	0.991	0.390	0.143
	$\phi^{(w)}(z)$	$4.99 \cdot 10^{-13}$	$1.92 \cdot 10^{-13}$	$7.56 \cdot 10^{-14}$	$2.78 \cdot 10^{-14}$

an argon atom outside NaCl, assuming the ions of the latter to attract like argon atoms are also included. This latter assumption probably gives an over-estimate of the effect of the van der Waals' forces, as the Na ions are like neon and not like argon. Two other cases have therefore been considered, *viz.*, argon outside KCl and neon outside NaF, in one case all the electronic systems being like argon, in the other all like neon. The final results are given in Table IX.

TABLE IX.—POTENTIAL FIELD OF NEON OUTSIDE NaF AND OF ARGON OUTSIDE KCl (ERGS).\*

$$* \alpha_{\text{NaF}} = 4.62 \text{ \AA.} \quad \alpha_{\text{KCl}} = 6.28 \text{ \AA.}$$

	$z/a$	0.5.	0.7.	1.0.	1.5.
Neon and NaF	$\phi^{(e)}$	$6.54 \cdot 10^{-13}$	$1.10 \cdot 10^{-13}$	$7.65 \cdot 10^{-13}$	$9.00 \cdot 10^{-17}$
	$\phi^{(f)}$	$9.16 \cdot 10^{-13}$	$2.58 \cdot 10^{-13}$	$1.25 \cdot 10^{-13}$	$1.72 \cdot 10^{-22}$
	$\phi^{(w)}(s = 5)$	$7.75 \cdot 10^{-14}$	$4.74 \cdot 10^{-14}$	$2.96 \cdot 10^{-14}$	$1.82 \cdot 10^{-14}$
Argon and KCl	$\phi^{(e)}$	$4.81 \cdot 10^{-13}$	$8.10 \cdot 10^{-14}$	$5.63 \cdot 10^{-13}$	$6.61 \cdot 10^{-17}$
	$\phi^{(f)}$	$2.06 \cdot 10^{-14}$	$5.80 \cdot 10^{-13}$	$2.80 \cdot 10^{-13}$	$3.86 \cdot 10^{-22}$
	$\phi^{(w)}(s = 5)$	$2.15 \cdot 10^{-13}$	$1.31 \cdot 10^{-13}$	$8.20 \cdot 10^{-14}$	$5.04 \cdot 10^{-14}$
	$\phi^{(w)}(s = 6)$	$2.87 \cdot 10^{-13}$	$1.10 \cdot 10^{-13}$	$4.35 \cdot 10^{-14}$	$1.60 \cdot 10^{-14}$

For the same reason the force on neon outside NaF and the force on argon outside KCl have been calculated.

TABLE X.—FORCE ON NEON OUTSIDE NaF AND ON ARGON OUTSIDE KCl (IN DYNES).

	$z/a$	0.5.	0.7.	1.0.	1.5.
Neon and NaF.	Electrostatic	$1.26 \cdot 10^{-4}$	$2.11 \cdot 10^{-5}$	$1.47 \cdot 10^{-6}$	$1.72 \cdot 10^{-8}$
	Polarisation	$5.29 \cdot 10^{-4}$	$1.48 \cdot 10^{-7}$	$7.11 \cdot 10^{-10}$	$9.89 \cdot 10^{-14}$
	V. d. Waals ( $s = 5$ )	$5.46 \cdot 10^{-6}$	$2.11 \cdot 10^{-8}$	$8.60 \cdot 10^{-7}$	$3.31 \cdot 10^{-7}$
Argon and KCl	Electrostatic	$6.80 \cdot 10^{-5}$	$1.14 \cdot 10^{-5}$	$7.94 \cdot 10^{-7}$	$9.30 \cdot 10^{-9}$
	Polarisation	$4.74 \cdot 10^{-6}$	$1.33 \cdot 10^{-7}$	$6.36 \cdot 10^{-10}$	$8.85 \cdot 10^{-14}$
	V. d. Waals ( $s = 5$ )	$1.11 \cdot 10^{-5}$	$4.28 \cdot 10^{-6}$	$1.75 \cdot 10^{-6}$	$6.70 \cdot 10^{-7}$
	( $s = 6$ )	$2.84 \cdot 10^{-5}$	$7.00 \cdot 10^{-6}$	$1.88 \cdot 10^{-6}$	$4.58 \cdot 10^{-7}$

A simple application of these figures has been made to calculate the heat of adsorption of argon on KCl. Using the repulsive force constants of former papers,<sup>16</sup> a rough calculation shows the equilibrium distance to be about  $6a$ . The corresponding value of  $\phi$  is  $1.6 \cdot 10^{-13}$  ergs, so that the heat of adsorption of one gram molecule (neglecting the influence of the molecules on each other) is about 2000-2500 calories. This is of the order of observed heats of adsorption.<sup>17</sup>

The results can be further applied to estimate the concentration of atoms in the neighbourhood of a solid by Boltzmann's formula ( $v = v_0 e^{\phi/kT}$ ). Assuming an inverse fifth power attraction, the indication is that the concentration of argon at a distance of 10 Å from KCl is about two to three times the normal at room temperature.

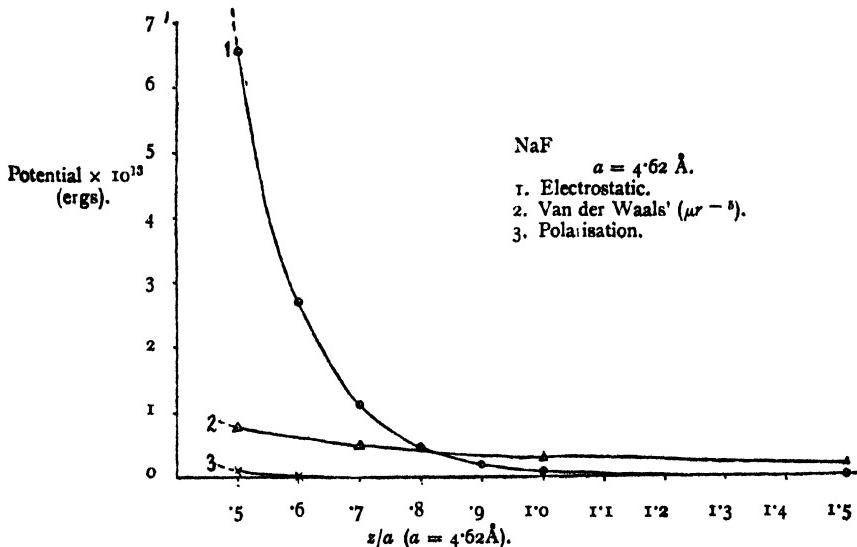


FIG. 2.—The Potential Field outside a (100) plane of NaF on (1) a charged particle, (2) on Neon.

<sup>16</sup> Roy. Soc. Proc., A vol. 112, p. 230 (1926), etc.

<sup>17</sup> Nitrogen on charcoal is 4740 cals. per gram molecule (Gregg, Journ. Chem. Soc. (1927), p. 1507).

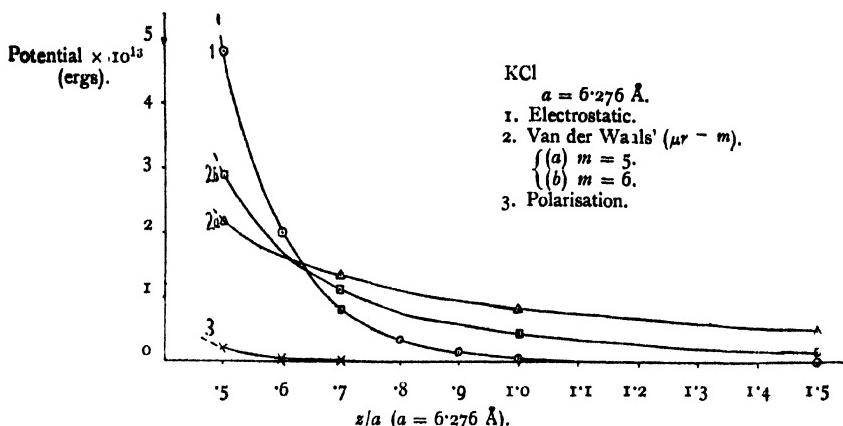


FIG. 3.—The Potential Field outside a (100) plane of KCl on (1) a charged particle, (2) on Argon.

## THE LAW OF MOLECULAR FORCES.

By ALFRED W. PORTER.

*Received, 28th December, 1927.*

The subject of molecular forces is a somewhat elusive one; many attempts have been made to derive a knowledge of it from experimental results, and yet there is no certain knowledge concerning it at the present day.

The first attempt (probably) was made by Young who realised that the breaking tension of a material must be a lower limit to the attraction per unit area between the molecules.

A more serious consideration of the subject was undertaken by Laplace, who, however, limited the problem to the case in which matter could be regarded as a *continuum*. He calculated the pressure that must exist in a fluid or solid in consequence of the attractions between the molecules. This can be obtained most easily by calculating the force of one elementary volume on a lamina; then, by integration, on all the lamina which build up one-half of the body. From this by integration find the force of the half-body on a unit area lamina and finally on all such lamina constituting the other half of the body. The result is the internal pressure,  $K$ , in so far as it arises from attractions. The result for an assumed force  $\Gamma mm'/r^n$  between elementary volumes is

$$K = \Gamma \frac{2\pi\rho^2}{(n-1)(n-3)(n-4)} \left[ -\frac{1}{x^{n-4}} \right]_0^\infty \quad . \quad . \quad . \quad (1)$$

Here  $\rho$  is the density, and  $\Gamma$  an attraction constant (analogous to the gravitation constant). This expression becomes infinite either for  $x = \infty$  or  $x = 0$  whatever the value of  $n$  assumed. (Other functions can be found for which this is not the case; for example an exponential law.) On this account Lord Rayleigh, who devoted much time to the problem, saw nothing promising in a power law. He did not, however, advance beyond the fundamental assumptions of Laplace. In a letter to me he expressed hesitation in extending the investigation so as to bring it more nearly into

unison with the *molecular* theory of matter. Though he did not go fully into the question the impression conveyed was that he shrank from tackling the thermal questions which must arise when not only the positions but the motions of the molecules are taken into account. It may be observed that from Laplace's standpoint neither  $K$  nor the surface tension  $T$  which can be calculated from it would vary with temperature unless a special factor be arbitrarily introduced to allow for their variations.

The most important advance<sup>1</sup> consisted in recognising that on the molecular theory no two layers can approach to a less distance apart than the molecular diameter,  $\sigma$ . If the lower limit be taken as  $\sigma$  a power law gives

$$K = \Gamma \frac{2\pi\rho^2}{(n-1)(n-3)(n-4)} \frac{1}{\sigma^{n-4}} \quad \dots \quad \dots \quad (2)$$

From this the surface tension can be obtained by equating the work done in separating the two halves of the body and dividing by the total fresh area formed thereby. This gives

$$\text{Surface tension} = T = \frac{\Gamma\pi\rho^2}{(n-1)(n-3)(n-4)(n-5)} \frac{1}{\sigma^{n-5}} \quad (3)$$

(at least provided that  $n > 5$ ).

By dividing (2) by (3) we eliminate the attraction constant and obtain

$$\frac{K}{2T} = \frac{n-5}{\sigma}.$$

This last step was taken by Edser,<sup>2</sup> and also by the present writer (in his lectures since 1916). If applied to water for which  $K = 12500$  Atm.,  $T = 75$  dynes/cm.,  $\sigma = 4 \times 10^{-8}$  cms., one obtains  $n = 8.33$ .

The corresponding value of  $\Gamma$  is of the order of  $10^{-22}$ .

The distances,  $D$ , at which gravitation and molecular forces would be about equal to one another for different powers are as follows:—

$n$	5	6	7	8
$D$	600	1	$5 \times 10^{-2}$	$7 \times 10^{-3}$ cms.

A large number of other substances yield nearly the same value of  $n$ ; and one might very plausibly be misled into considering the problem as solved.

Further consideration has convinced me, however, that that value is erroneous because the assumption made in obtaining (2) and (3) must give only very crude values for  $K$  and  $T$ . Though the two halves of the body are supposed never to approach to a less distance than  $\sigma$  the matter is still regarded as being otherwise continuously distributed. This means that each layer is supposed to be placed at a greater distance than its actual value when gathered up into molecules. Both  $K$  and  $T$  are therefore too small. In fact calculations made for me by Mr. V. Thatte by summing up the effects of individual molecules gives for  $K$ , when  $n$  is 7, a value about twelve times greater than is given by (2). Although a similarly large error must be attributed to formula (3) for the surface tension and the ratio is probably not as much in error, yet obviously the results are too crude for reliance to be placed upon them.

<sup>1</sup> Sutherland, Bakker, Kuenen, *Die Zustandsgleichung, etc.*

<sup>2</sup> Fourth Colloid Report, British Association, 1922.

### Van der Waals' Equation of State.

Van der Waals considered that his intrinsic pressure term,  $a\rho^2$ , was independent of the law of force. His argument is very plausible; but he did not sufficiently recognise the predominant importance of the interaction of *adjacent* molecules. Taking two elements in the fluid a fixed distance apart, halving the density may not merely reduce the number of molecules in the element to one-half: it may reduce it to zero. In fact his argument will apply at most to cases in which each element contains at each density a sufficiently large number of molecules for average values to have a meaning and to be sensibly uniform over the element.

Mellor<sup>3</sup> gave a proof that Van der Waals'  $a\rho^2$  really involves the inverse fourth power. It may be put, adopting Kuenen's method as follows: Select any two molecules which are members of two groups, one on each side of a surface of separation. The force between them is assumed to be inversely as the  $n$ th power of their distance apart. Draw the surface separating them. The line joining them has a definite direction with respect to this surface. Now change the density of the gas. The distance between each particular pair of molecules increases to  $\kappa$ -fold its original value; moreover the line joining them preserves its direction unchanged. The separating surface changes in the ratio  $\kappa^2$ . Hence the contribution to the total force per unit area from *each* pair changes in the ratio  $\kappa^{-n-2}$  and the volumes in which the groups of particles lie change as  $\kappa^3$ . Hence the force per unit area across the interface due to all the pairs changes as  $v^{-(\frac{n+2}{3})}$ . According to van der Waals this is  $v^{-2}$ ; hence  $n = 4$ . Even if this argument be accepted as valid the law remains uncertain on account of the uncertainty of the equation itself. If this law is adopted equation (2) would need to be altered by replacing  $\frac{1}{(n-4)}\sigma^{n-4}$  by  $\log R - \log \sigma$  where  $R$  may be taken as representing the average dimensions of the body. In this case  $K$  would increase slowly with the size of the body. There is nothing known against such an increase being true in reality. Indeed, if gravitation is the residual molecular attraction at comparatively great distances such an increase is certainly true.

Clausius showed that  $a$  must vary according to an inverse function of the temperature. This may be a consequence of the motions of the molecules altering the effective distance  $\sigma$ .

The equation of van der Waals is only a fair approximation to the behaviour of real gases, involving deviations amounting to 30 per cent. It is not safe therefore to rest much upon the numerical values or exact form of the "small term"  $a/v^2$ .

### Viscosity.

Some information may be obtained from the variation of the viscosity of gases with temperature. Sutherland showed that the effective diameter of a molecule in collision is increased by the existence of attractions between it and its neighbours. Molecules which otherwise would not collide are swept in comet-like paths and the resulting change of momentum is equivalent to a collision. The effective diameter  $\sigma$  is connected with the "real diameter"  $\sigma_0$  by the relation

$$\sigma^2 = \sigma_0^2 \left( 1 + \frac{C}{T} \right),$$

<sup>3</sup> *Phil. Mag.*, III., p. 423 (1902).

where C is calculable from considerations of energy and angular momentum under the attracting force. This factor C is Sutherland's constant; it can be obtained from experiments on viscosity.

Now experimentally, from viscosity measurements, C comes out to be of the order of the critical temperature,  $T_c$ . We may compare its value with the value of  $T_c$  obtained from van der Waals' equation according to which

$$T_c = \frac{8}{27} \frac{a}{b\kappa} = \frac{8}{27} \frac{K}{\kappa b\rho^2}$$

where  $\kappa$  is the gas constant per molecule.

Taking equation (2) for  $K/\rho^2$  we have

$$\frac{2}{3} \frac{\Gamma}{(n-1)\sigma_0^{n-1}\kappa} = \frac{8}{27} \frac{K}{\kappa b\rho^2}$$

$$\frac{8}{27} \frac{\Gamma \cdot 2\pi}{\kappa b(n-1)(n-3)(n-4)\sigma_0^{n-4}}$$

or remembering that  $b$  is proportional to  $\frac{\pi\sigma_0^3}{6}$ , say,  $f \frac{\pi\sigma_0^3}{6}$ ,

$$(n-3)(n-4) = \frac{8 \times 12 \times 3}{27 \times 2f} = \frac{16}{3f}$$

whence  $n = \frac{7}{2} \pm \sqrt{\frac{49}{4} - 12 + \frac{16}{3f}} = \frac{7}{2} \pm \sqrt{\frac{1}{4} + \frac{16}{3f}}$ .

If  $f$  be taken as unity  $n \doteq 5.9$

The fact must be faced, however, that van der Waals'  $a$  varies inversely with the temperature (Clausius), and unless a similar variation be attributed (somewhat arbitrarily) to  $K$  the value so calculated is quite unreliable. Sutherland inferred from the behaviour of gases that  $n = 4$  satisfied the experimental values quite well.

### General.

It is evident that not much is to be expected from simple considerations based on gas laws. In the case of solids when the molecules are considered and their effects are summed up instead of integrated there is more likelihood of success, but even then difficulties will arise in consequence of the motions of the molecules.

## A BRIEF REVIEW OF A STUDY OF COHESION AND CHEMICAL ATTRACTION.

BY THEODORE W. RICHARDS, HARVARD UNIVERSITY.

*Received 11th November, 1927*

The present research concerning the action of cohesive and chemical affinity was begun nearly thirty years ago. Its method has been primarily inductive. That is to say, no assumption was made beforehand as to the nature of the agencies at work. The guiding hypothesis and mathematical

treatment were developed from the actual behaviour of matter. For it may well be that matter possesses intrinsic potentials which cannot be discovered except by the study of matter itself.

Although no proof had previously been offered by anyone, it had often been assumed that chemical affinity and cohesion pull atoms and molecules together by attracting forces. This probability was suggested by Newton long ago.<sup>1</sup>

If forces come into play, pressure must be exerted upon the "atomic surfaces" (whatever these may be), by the action of these forces. Furthermore, these "surfaces" between the atoms in a compound are probably the same kind of boundaries as those functioning between colliding molecules in gases. There is, of course, no need (except for convenience in explanation) to imagine any actual "surface" of an atom; one needs merely to imagine a repellent force which resists the attracting force in the one case, or the momentum in the other. In other words: the same resisting forces must come into play in the transitory collisions in gases as in the union of two atoms in compounds.

That the kinetic collision between molecules of gases is not a collision between hard, incompressible particles (as van der Waals assumed), was suggested to me in 1899 by a fact noted even by van der Waals himself,—namely, that the so-called "constant"  $b$  is really variable under great pressure. If  $b$  is variable, must not the practical volume of the atom also be variable? This "practical volume" of the atom is that which marks its relations with other atoms; we have indeed no other mode of estimating it. Since it diminishes under great pressure, the practical volume of the atom must be considered as compressible.

But why, if this is the case, is the  $b$  of van der Waals ever constant? In gases and vapours there must be large empty spaces between these practical volumes, such as the kinetic theory of gases demands. In any given gas at any given temperature, the average momentum of collision between particles would be independent of external pressure, until the bulk of the liquid is approached. Hence below (let us say) 150 atmospheres  $b$  is fairly constant. But when the total volume is still further diminished, the intrinsic repelling tendency begins to become perceptible; and as this yields to the great pressure,  $b$  is diminished. Thus many of the deviations of the equation of van der Waals from exact fulfilment are explicable.

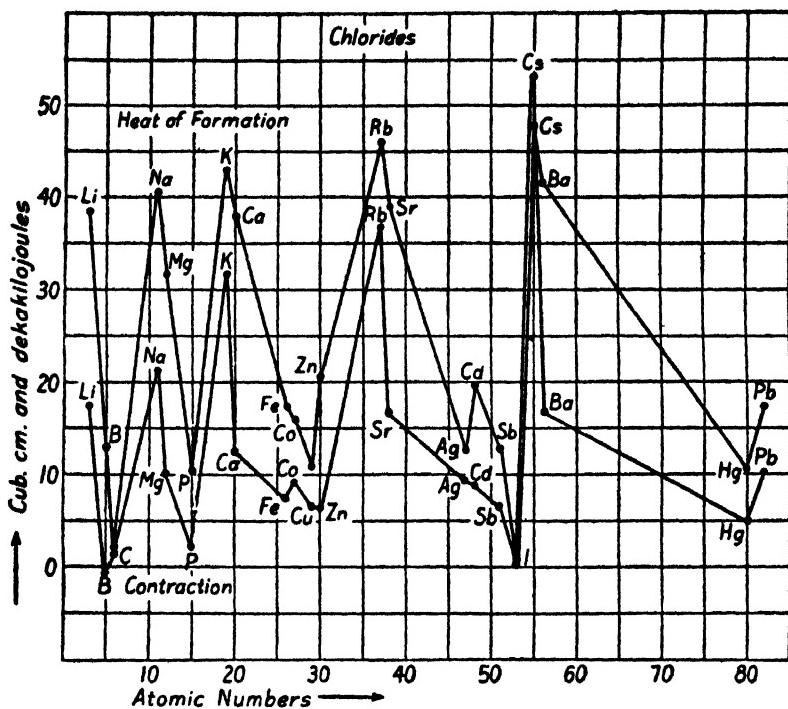
The next step in the train of thought is obvious. If changes in the practical volumes of the atoms and molecules are to be inferred even from gases, may not they be detected even more markedly in the behaviour of solids and liquids? That is, chemical affinity and cohesion must likewise produce differing effects according to their intensities, if these forces produce pressure. Great affinity should produce great compression, small affinity small compression. If these phenomena exist, evidence would be afforded both that pressure is produced by affinity and that the practical

<sup>1</sup> A brief history of the whole subject has been published in *Chemical Reviews*, **2**, 315 (1925). This contains many references to the work of others, as well as to the earlier part of the present research. Perhaps the most important of the present series are the following: *Proc. Amer. Acad. of Arts and Sci.*, **37**, 399 (1902); *Z. physik. Chem.*, **40**, 597 (1902); *Proc. Amer. Acad. of Arts and Sci.*, **39**, 579 (1904); *Zeit. physik. Chem.*, **49**, 15 (1904); *J. Chem. Soc.*, **99**, 1201 (1911) (Faraday Lecture); *J. Amer. Chem. Soc.*, **36**, 2417 (1914); **46**, 1419 (1924); **47**, 731 (1925); **48**, 3063 (1926). Since 1902 the investigation has been generously subsidized by the Carnegie Institution of Washington, as well as by other research funds, assistance indispensable for its prosecution.

A moderately condensed but comprehensive discussion (much more detailed than the present one), will appear in the *J. de Chimie Physique* of January or February, 1928.

volumes of the atoms are compressible. The most obvious means of verification lay in the comparison of contractions which occur when different metals possessing widely different affinities combine with some one very compressible non-metallic substance such as chlorine.

Accordingly, a comparison was made of the heats of reaction (which roughly, although not exactly, indicate relative affinities) with the change in volume occurring on the synthesis of several chlorides. Figure 1 shows the results of this comparison. There can be no doubt that where the affinities are great the contractions also are great: a striking confirmation of the inference.



Comparison of heat evolved with contraction occurring during formation of equivalent quantities of chlorides. The upper zigzag line indicates the heat of formation; the lower zigzag line, the corresponding contractions in cubic centimetres.

FIG. I.

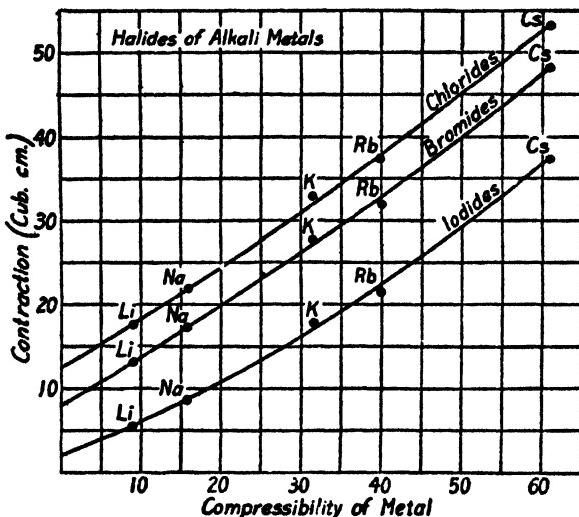
Afterwards it was found that other generalisers, especially Müller-Erzbach in 1881 and Traube in 1899, had observed this parallelism, but without drawing the conclusions herewith detailed.

Indeed, suggestive as it is, this study was not alone a sufficient basis for proof of the inference; because change of volume is determined (as implied above) by two factors, pressure, and compressibility, which latter no one up to that time had considered at all in this connection.

These thoughts led to the determination of many compressibilities; of which only very few were previously known, and those but poorly determined. A new exact method was devised by which the compressibilities of various elements and compounds were determined through direct comparison

with that of mercury. Several interesting facts were discovered from the data thus secured. In the first place it was found indubitably that with similar affinities greater compressibility usually involves greater change of volume in the formation of chemical compounds. The study of Figure 2 is enough to indicate this important relation. It forms a very striking support to (although not an indubitable *proof of*), the idea that chemical affinity (in this case polar), exerts pressure, and that this pressure is resisted by an opposing repulsive pressure, which finally balances the compressing effect.

A further striking fact demonstrated by these compressibility determinations was that the curve showing the relative compressibilities of solid elements is almost parallel with that of atomic volumes (Fig. 3). The bulky elements, then, in which cohesion is slight, are very compressible; and the compact, dense, and comparatively non-volatile elements are but slightly compressible. In other words, substances which are already greatly compressed are not easily compressed further, which seems only common



Graph depicting the compressibilities of the alkali metals compared with the contraction during the formation of their halides. Contraction on combination in cubic centimetres per mol is plotted ordinately; compressibilities ( $\times 10^4$ ) of the elements are plotted as abscissæ.

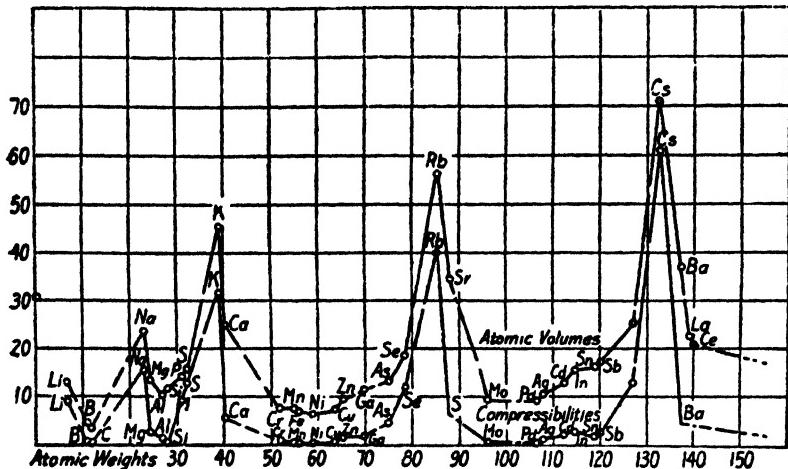
FIG. 2.

sense. Hence, also in the non-polar action of cohesion the "Practical volume" of the atoms seems to be in part determined by the pressures of affinity (this time cohesive affinity).

For convenience in thinking, then, the practical volume of the atom and molecule, in all three states of matter, may be pictured as compressible. This practical volume is simply in a given case the bulk actually occupied in solids and liquids under definite conditions. For a single atom it would be the atomic volume divided by Avogadro's number.

There is not space here to discuss in detail the confirmatory researches which found that (other things being equal) substances with high boiling-points usually have relatively smaller volumes, greater surface tensions, lesser compressibilities and coefficients of expansion, greater molecular heats of vaporisation, and greater refractive indices than similar substances with lower boiling-points. Table I. illustrates these relations, all of which are consistent with the theory of the balance of pressures. For comparison,

isomers are best employed; extraneous complications often present, are then less serious. In other words, the facts are remarkably consistent with the postulate that both chemical affinity and cohesion not only hold the



Atomic volumes and compressibilities of solid elements, plotted in relation to atomic weights. The upper line gives the familiar atomic volume curve of Lothar Meyer; the lower line records the compressibilities of a number of solid elements determined at Harvard. Atomic volumes and compressibilities are both plotted as ordinates, the numbers indicating, respectively, cubic centimetres per gram-atom and compressibilities multiplied by 1,000,000. Atomic weights are plotted as abscissæ.

FIG. 3.

atoms together but also *pull* them together. Both these agencies then must exert pressure. The facts further indicate that there must be some distending pressure or pressures to withstand these intense compressing agencies. No other explanation seems to fit the case.

TABLE I.—CORRELATION OF PROPERTIES.

	Ortho Xylene.	Meta Xylene.	Para Xylene.
Density . . . . .	0·8811	0·8658	0·8611
Compressibility $\beta \times 10^6$ . . . . .	61·2	64·8	67·5
$(\Delta\beta/\Delta\rho) \times 10^6$ . . . . .	4·5	4·7	4·9
Coefficient of expansion $\times 10^6$ . . . . .	973	994	1009
Boiling-point . . . . .	144·0	139·0	136·0
Mol. heat of vaporisation (cal.) . . . . .	8·75	8·71	8·60
Surface tension (Mg./mm.) . . . . .	3·09	2·96	2·92
Refractive index . . . . .	1·5078	1·5002	1·4985

These ideas are not entirely new, although they have been approached in a new way. Young, Rayleigh, and others, conceived of a balance of opposing, non-polar pressures; but none had followed out completely the consequences, especially as regards chemical change.

When a molecule is composed of more than one atom, different intrinsic internal pressures must evidently exist on different sides of each atom, except, perhaps, in cases like sodium chloride. For instance in liquid bromine

(which boils under atmospheric pressure at about  $60^{\circ}$ , but does not dissociate appreciably below red heat), evidently the two atoms in a molecule are bound together much more firmly than in the mere cohesion of the liquid. Hence much greater pressure (and therefore much greater compression) must exist between the atoms of a given molecule than exists between two different molecules. The first-named pressure, the greater one, may be called chemical intrinsic pressure; the second, the smaller one, may be called cohesive intrinsic pressure. They are both probably due in this case (as in others) to the same forces being exerted to different extents. In such cases the atomic fields of force must be distorted, the atomic structure being far more compressed on one side than on all the other sides. This situation may be illustrated by Fig. 4.

Such is the rough outline of a theory which seems able to explain many of the properties of matter. Indeed I have not yet found any pertinent phenomenon which is not more or less elucidated by its tenets and corollaries. Nor have I yet heard of any valid objections to it. If, however, an hypothesis explains merely the properties on which it was based, nothing is proved. Such an eventuality is a matter of course, if the induction has been properly carried out. But the present hypothesis explains many other facts besides those upon which it was built. For example, it helps greatly in understanding why some substances are hard and others soft; why some

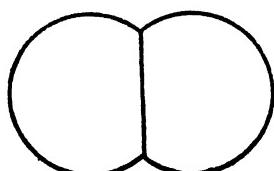


FIG. 4.—Molecule of bromine. Showing compression of atomic fields due to non-polar chemical pressure.

substances are tenacious and others hold weakly together; it gives a reasonable explanation of changes of volume occurring in crystals, especially isomorphous crystals composed of similar substances but of different atomic volumes. Furthermore, the idea of balanced internal pressures, different on different parts of "surfaces" of the atom gives an adequate picture of stereochemical phenomena. A carbon atom in combination must have four depressions on the "atomic surface." If these

are all unequal (that is, due to different affinities), the atom (or, if one prefers the atomic field of force), must be distorted into an asymmetric entity. One can see why any change in intensity of any one of these contacts would affect all the other three to a slight extent. Many aspects of the actual behaviour of carbon compounds become capable of interpretation on this basis. Metastable equilibrium (sometimes badly named "false equilibrium"), such as that which exists at ordinary temperatures between mixed oxygen and hydrogen gases, becomes easily comprehensible; so also do many aspects of catalysis, which is merely the release from an inhibition to react. The full discussion of these and other applications would take far too much space for the present communication. Many of them have been already discussed in sundry papers in the past. Some of them are briefly explained in a paper soon to appear in the *Journal de Chimie Physique*.

Suggestive as such partly qualitative explanations may be, they are not, of course, final. The problem involved in the mathematical analysis of the fundamental idea was difficult on account of the many variables involved, but nevertheless worth attempting. Reasonable certainty in such a case is not to be attained without mathematical evidence.

Evidently the main influences which work in any physicochemical atomic contacts may be represented by the following equation of two terms indicating compressing agencies, with two terms indicating distending agencies:—

$$\mu + \Pi = \Pi_\mu + P_\theta \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which  $\rho$  represents external pressure,  $\Pi$  the sum of all possible intrinsic compressing effects;  $\Pi_\rho$  the intrinsic distending or "repulsive" pressure, and  $P_\theta$ , thermal pressure. This equation is expressed as between pressures rather than forces because the first and the last terms may then be directly measured; for  $\rho$  may be found by an ordinary pressure gauge, and  $P_\theta$  equals  $T\alpha/\beta$  where  $\alpha$  and  $\beta$  are coefficients of expansion and compression respectively.<sup>2</sup> The steps of reasoning by which these rather obvious conclusions were reached are detailed elsewhere.

All the terms of Equation 1 must be variable. The variations in  $\rho$  and  $P_\theta$  may be measured, and therefore need not be entered in the expression. Those of  $\Pi$  and  $\Pi_\rho$  remain to be discovered. Common observation of the phenomena of cohesion and chemical combination shows that both  $\Pi$  and  $\Pi_\rho$  must decrease as the distance of the particles (or the volume of the system) increases. Thus we may write for a solid or liquid with monatomic molecules :—

$$\rho + \Pi_0 \left( \frac{v_0}{v} \right)^m = \Pi_\rho \left( \frac{v_0}{v} \right)^n + T\alpha/\beta \quad . \quad . \quad . \quad (2)$$

while admitting that the exponents  $m$  and  $n$  are not necessarily constant.  $n$  must be larger than  $m$ , otherwise the system could not adjust itself to equilibrium, and a slight increase of external pressure would cause the solid or liquid to collapse.<sup>3</sup>

This fundamental equation, on the consolidation of its second member and on differentiation, yields a simple expression in which the internal pressure is shown to be the reciprocal of the product of the compressibility and the difference between the two exponents :

$$\Pi_0 = \frac{1}{\beta(n' - m)}.$$

With the help of the experimental value of thermal pressure and other considerations too lengthy to be given here, a somewhat similar expression in terms of the coefficient of expansion is easily found. Heats of evaporation indicate that the exponent  $m$  is probably not far from 2, as van der Waals assumed, and the other exponent ( $n$ ) may likewise be evaluated (in a somewhat complicated way) with reasonable probability.<sup>4</sup>

The outcome makes it possible to compute many properties of an isotropic substance. For example, the effect of pressure on compressibility may be calculated within the limit of experimental error. Hence the mathematical theory is supported.

Moreover, these equations make it possible to compute (from my own results as well as from the admirable experimental work of Percy W. Bridgeman), the actual internal pressures existing in monatomic substances. A few examples are given in the following table (sec p. 118).

These pressures, although they are very large, are nevertheless, not unreasonable. Certainly their relative magnitudes correspond more or less satisfactorily with the volatilities, hardness, and other properties of the substances. Tungsten, being the least volatile of all, should have (as it has)

<sup>2</sup> The exact definition of  $P_\theta$  would require too much space for this brief review. The approximation above (often perhaps within 15 per cent.), serves amply for the present purpose.

<sup>3</sup> Somewhat similar equations were offered by Mie in 1903 and Gruneisen in 1912, both after the beginning of the present research. They differ in important ways, however, from the present method of treatment. For references and discussion see the article in *Chem. Rev., loc. cit.*

<sup>4</sup> *J. Amer. Chem. Soc.*, 48, 3063, 1926.

TABLE II.

ESTIMATES OF INTRINSIC COHESIVE PRESSURES OF SEVERAL ISOTROPIC ELEMENTS  
TOGETHER WITH APPROXIMATE THERMAL PRESSURES AT 20° C.

	$P_\theta$ .	$\Pi_\theta$
Potassium . . . . .	2,100	15,300
Sodium . . . . .	4,000	33,000
Mercury . . . . .	13,100	41,300
Lead . . . . .	10,340	72,000
Aluminium . . . . .	14,000	191,000
Silver . . . . .	16,120	208,000
Gold . . . . .	21,800	243,000
Copper . . . . .	19,390	376,000
Platinum . . . . .	21,000	465,000
Iron . . . . .	16,600	587,000
Tungsten . . . . .	13,400	1,100,000

(N.B.—The unit of pressure is the megabar = 0.987 atmosphere.)

the greatest internal pressure. Even the absolute magnitudes receive confirmation from other facts. If, as is generally conceded, the molecules of rather low boiling organic liquids cohere with a pressure of several thousand atmospheres, it is not surprising that mercury and sodium, for example, should have internal pressures ten times as great. And Griffith has found from his extrapolation of the actual breaking stress of fine glass fibres that over 100,000 atmospheres are probably here required. Moreover, the values of the internal pressures given in the above table run approximately parallel to Young's moduli (which indicate tenacity), being on the average about one-third as large as the latter when reduced to the same area of cross-section. Obviously, the bearing of the new results on the theory of elasticity is interesting and worthy of expansion.

The comparatively simple mathematical treatment thus far discussed applies only to monatomic elements.<sup>5</sup> As already indicated, chemical combination, in polyatomic elements or compounds, involves much more complicated treatment. In such cases, which constitute the vast majority of substances, the measured values of  $\alpha$  and  $\beta$  are weighted averages of very small quantities pertaining to the greatly compressed portions of the atoms within the molecule, and larger quantities pertaining to the far less compressed periphery of the molecule which borders on another similar periphery. Thus, for example, the compressibility of a binary compound may be roughly pictured by the following equation, in which  $x$  is the fraction of each atom subjected only to cohesive pressure  $\Pi_1$  and  $(1 - x)$  is the fraction subjected to the intense chemical pressure  $\Pi_2$ .

$$\beta \cong \frac{x}{n_1 - m} \left( \frac{x}{\Pi_1} + \frac{1-x}{\Pi_2} \right) . . . . . \quad (3)$$

A somewhat similar expression, of course, applies to  $\alpha$ .

Since this is the case, it follows that the thermal pressure,  $T\alpha/\beta$  of a compound is merely a compromise value, involving the various thermal pressures at the several atomic and molecular contacts. Without a further interpretation, the result has little significance, although it has been considered seriously by others.

There is not space here to discuss the probable value of the fraction  $x$ ,

<sup>5</sup> Incidentally, it should be added that equations containing the gas-constant R in this series of expressions hold only when  $C_v = 3R$ .

nor to enter into further details. Nevertheless, the importance of the idea which postulates the existence of different pressures on different sides of a single atom is of great importance. It does not seem to have been investigated, or in fact even mentioned, by others.

For example, the pressure between the two atoms of bromine forming a single molecule is probably of the order of 100,000 atmospheres, whereas the pressure between the different molecules in the liquid is probably of the order of 5000 atmospheres. Similar conditions must exist in organic compounds; thus, whereas in ethyl ether the cohesive pressure is probably of the order of 2000 atmospheres, the intrinsic chemical pressure existing between atoms of carbon and hydrogen or carbon and oxygen (different in each case) must be much over 100,000 atmospheres. Precisely the same sort of difference, although perhaps of less degree, must exist within anisotropic crystals, even when they are built up of only one kind of atom (*e.g.*, zinc).

Taking account of all these circumstances and of the numerical values assigned to the variables concerned, it appears that the actual heats of chemical reaction possess the order of magnitude demanded by the calculated pressures. In other words, both heats of evaporation and chemical heat appear to represent (as has been suggested by others) simply the nett amount of work done by affinity when atoms approach one another from a considerable distance.

When there are only two kinds of atoms present, some interesting conclusions can be drawn, if due account is taken of the composite nature of the system. Of course, with water the situation is uniquely complicated, because of changing polymerisation. The  $\alpha$  and  $\beta$  of this most common substance have no significance without corrections (as yet unknown) for the change of volume due to its changing molecular weight and volume.

That the exact mathematical equations for chemical compounds have not yet been derived need cause no surprise. The details of the situation are extremely subtle, the variables extremely numerous. These complications do not, however, indicate fault in the theory. They are necessary consequences of the nature of things, and are no more prejudicial to the general idea than the complications involved in the familiar three-body problem are to the theory of gravitation.

The internal pressures discussed in this paper are concerned with almost every property of matter in the solid or liquid state. Hence their elucidation is likely to assist in the interpretation of a wide variety of phenomena. The progress and outcome of untried organic reactions, for instance, may perhaps be capable of prediction. The simpler applications, indicated in this paper, have already been severely tested and not found wanting.

To the writer the theory of balanced pressures, although as yet far from complete in all of its countless ramifications, nevertheless seems to present a consistent and reasonable picture of the mode of action of the intrinsic affinities in matter. Some such theory as this, indeed, appears to be necessary to explain the action of cohesion and chemical affinity, to elucidate the great tenacity, hardness and impenetrability of many solids, and thus to explain the persistence of the framework of the universe. In very recent times modifications of it have been adopted by Lennard-Jones, and Born in their valuable contributions,<sup>6</sup> as well as by others. The chief differences of interpretation lie in the proportional part played by electrical

<sup>6</sup> Born, Max, Numerous papers, in particular *Ann. Physik*, 61, 87 (1919); also in *Der Aufbau der Materie*, Berlin, 1922, and *Atomtheorie des festen Zustandes*, Berlin, 1923; Lennard-Jones, J. E., *Proc. Roy. Soc.*, A 106, 709 (1924), etc.

attraction in the affinity pressure  $\Pi_0$ , as well as in the values of the exponents involved. The ingenious assumption made by Sir J. J. Thomson that all systems are wholly electrical, and that a fundamental change (indeed a reversal) of Coulomb's law occurs when the atoms are at close range, represents the electronic extreme.<sup>7</sup> A full discussion of these suggestive contributions would far exceed available space; but I venture to suggest that non-polar affinity is probably non-electrical and that it must be very great in such cases as metallic platinum and tungsten.

The underlying cause of non-polar attraction may be no more easily discoverable than that of gravitation; nevertheless the behaviour of this attraction is within the reach of inductive study. One cannot but feel that although much remains to be done, at least something has been accomplished by various investigators towards the fulfilment of Newton's parting injunction concerning chemical affinities: "It is the Business of Experimental Philosophy to find it out."

### Summary.

This paper contains a brief review of the main points in a series of about forty papers (1901-1926).

From the study of the volumes and compressibilities of solids and liquids, and the comparison of the energy changes with changes of volume during chemical reaction, it is concluded that both cohesion and chemical affinity exert pressure, and that this internal pressure tends to diminish the volume of the liquid or solid system concerned.

Many facts concerning not only volume, but also tenacity, hardness, ductility, crystal form, isomorphism, asymmetric carbon, metastable equilibrium, etc., support this conclusion.

The affinity-pressure may be either polar or non-polar, or both. The evidence is that the non-polar part may be often very great, e.g., in metallic platinum. The combined internal pressure thus produced appears to be too great to be resisted by thermal pressure alone. Therefore an intrinsic distending pressure in addition to thermal pressure must exist in atoms.

Hence every substance must exist as such by means of a balance of pressures:—external pressure plus affinity pressure equals intrinsic distending pressure plus thermal pressure.

Chemical affinity pressure must differ from cohesive pressure mainly in its intensity and in the fact that the chemical union of two atoms must involve great atomic distortion on one side of each, not equalled by the effect of the cohesive pressure around the periphery of the molecule.

Simple cases involving the above considerations have been subjected to mathematical analysis, with reasonably satisfactory results. Very high internal pressures in non-volatile solids are indicated, having the order of the breaking strength of very rigid substances like glass. These pressures are consistent with the heats of chemical combination and the heats of evaporation.

The theory seems to afford a consistent interpretation of the balance of forces which maintains the existence of chemical compounds, as well as of solids and liquids.

*Note.*—The most important of the original papers describing this study are, perhaps: *Proc. Amer. Acad. Arts and Sciences*, 37, 399 (1902); 39, 581 (1904); *J. Amer. Chem. Soc.*, 36, 2417; 46, 1419; 47, 731; 48, 3063. In footnote 1 many other references are given and made available. These papers and others have been correlated in a comprehensive article soon to be published by the *J. de Chimie Physique*.

<sup>7</sup> Thomson, Sir J. J., *The Electron in Chemistry*, p. 4 (Franklin Institute), Philadelphia, 1923.

# RESISTANCE TO SHEAR IN METAL CRYSTALS.

By G. I. TAYLOR.

*Received 22nd November.*

When a single crystal is strained so that it shears parallel to a crystal plane, the resistance to shear rapidly increases with the amount of shear and at the same time X-ray examination of the material shows that it has broken into fragments which remain crystals but are rotated through various small angles from the original orientation of the single crystal. It seems certain that the two phenomena are associated, but it is not at all clear how the breaking up of the crystals is responsible for the increased resistance to shear.

The theory most commonly put forward as an explanation is that in a perfect crystal a very small shearing force parallel to a crystal plane will cause all the atoms in one plane to slide over the atoms in the neighbouring parallel plane. The increased resistance to shear in an imperfect crystal is due to the fact that rows of atoms are held up at any imperfection in the crystal structure. This theory has many forms; the displaced material may for instance form keys in the crystal plane or, alternatively, the slipping may be held up at the boundaries between crystal fragments whose crystal axes are orientated at slightly different angles.

All such variations of the theory are identical in principle, and it seems to me that they all fail to do what is required of them. Suppose for instance that the crystal has only one set of parallel planes of slip, and suppose that it offers a very large resistance to cleavage across the planes of slip and a large resistance to compression. Under these circumstances a "key" between two neighbouring planes of atoms would lock them together completely over their whole extent whatever their area might be. When a "key" had formed between every neighbouring pair of planes the material would seize up completely. If the number of keys per unit volume depends on the amount of distortion and not on the size of the specimen, then an obvious consequence of the theory would be that large specimens would seize up more quickly than small ones. This is certainly not the case.

In the form of the theory which assumes the slipping to be held up at the boundaries of crystal fragments into which the single crystal is divided, the difficulty is more pronounced still, for the material would in that case be completely locked or seized up as soon as any breaking at all had occurred.

One must therefore assume that if the distortion is due to slipping parallel to crystal planes, more than one crystal plane is involved. In crystals of cubic symmetry like aluminium the symmetry alone shows that there must be many planes crystallographically similar to any plane of slipping, and these must also be planes of slip.

As soon as the possibility of slipping parallel to a number of crystal planes is admitted, the whole theory falls to the ground. Taking the case of aluminium for instance, there are twelve possibilities of slipping, namely, four planes of slip and three directions on each plane. By combining a

limited number of these it is possible for a crystal in any orientation to suffer a distortion identical with that of the main body of the original single crystal when sheared parallel to one crystal plane of slip. The shearing force necessary to produce this distortion is of course least when the crystal axes of the fragment are parallel to those of the main body of the crystal, but mathematical analysis shows that however the fragment is orientated, the resistance to shear parallel to the plane of slip of the main body of the crystal cannot be greater than about twice the minimum value.

It appears therefore that however favourably the fragments are orientated for increasing the resistance to shear, they cannot increase it to more than twice the resistance of the original single crystals, and if the actual distribution of crystal axes found from X-ray measurements is taken into account it is found that the increase in resistance to shear cannot amount to more than two or three per cent. of the original resistance of the unbroken crystal.

For these reasons I do not think that the breaking up of the crystal can be used to explain the increase in resistance to shear which occurs when a single crystal specimen of a metal like aluminium is distorted if the force necessary to move one plane of atoms over its neighbour is assumed to be small. The only alternative seems to be to imagine that this force is not small, but that there are regions in the material where a high concentration of stress can occur so that very high values of the shear stress can be reached locally although the mean shear stress is small.

The idea that stress may be concentrated at the end of a crack is an old one. It has been used with great success by Dr. A. A. Griffith in discussing the strength of glass, and earlier by Professor Inglis in another connection. It has, I think, been recognised among workers with single crystals of metals that there is a possibility that concentrations of stress may occur, but I do not remember seeing any attempt to explore the possibilities which this concentration afford for explaining the phenomena observed when single crystal specimens are distorted.

There are three things which require explanation:—

(1) The form of the load-extension curve, *i.e.*, the rapid increase in resistance to shear with increasing distortion.

(2) The fact that a certain definite proportion of the energy used in producing the distortion is absorbed in the material, the remainder being dissipated in the form of heat. As the shear strength of the material increases the amount of energy necessary to produce a given distortion increases. The amount of energy absorbed in the material also increases and in the same ratio.<sup>1</sup>

(3) The distribution of the crystal fragments.

I will take number 3 first. Up to the present not much information is available. Some years ago I believe Professor Joffé made some experiments with rock-salt which he bent. He came to the conclusion that fragments of the material broke away from the rest and acted like rollers, rotating about axes in the plane of slipping and transverse to the direction of slip. I do not know whether experiments have been carried out to see whether a similar type of breaking up occurs in metal crystals. Dr. Goucher in the course of X-ray examination of strained Tungsten crystals observed that the spreading of the fragments was due to rotation about a single line

<sup>1</sup> "Heat developed during plastic extension of metals," Farren and Taylor, *Proc. Roy. Soc., A.*, 107, 436.



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transverse to the length of his specimen. The distortion of his specimen was however very non-uniform, and he attributed, correctly I imagine, the spreading he observed to a curvature of the whole plane of slip which would make the orientation of the crystal fragments different on the two sides of his specimen.

No experiments seem to have been made in which precautions have been taken to ensure that the distortion of the specimen as a whole is uniform.

In the course of some experiments on the behaviour of Aluminium crystals under compression the distortion of a certain specimen was examined completely and proved to be uniform and to be due to slipping parallel to a crystal plane of type (111).<sup>2</sup> This specimen was cut parallel to the plane of slip, as calculated from measurements of marks on the surface of the specimen. It was ground and etched till the effect of the saw cuts had disappeared. This was verified by applying the same treatment to an undistorted specimen. The X-ray reflections in this case were perfect ones.

The specimen was then mounted on an X-ray spectrometer and exposed to a narrow beam of homogeneous X-rays from an iron anticathode. The beam was limited by passing through two small circular holes. Two sets of photographs were taken (*a*) with the axis of rotation of the spectrometer table in the plane of slip and transverse to the direction of slip, and (*b*) with the axis of the spectrometer table lying along the direction of slip. The exposures were each of 8 minutes' duration, and the intensity of the incident beam was kept constant while each set was being taken. Before each exposure the photographic plate was lowered in a vertical slide through a few millimetres, and the table was turned till the plane surface of the specimen was parallel to the axis of the beam of X-rays. Under these circumstances the direct beam produced a semi-circular spot which marked the position of the incident beam.

A series of exposures were made, the setting angle of the spectrometer table being increased by one degree from one exposure to the next. In this way the photographs shown in the accompanying figure were made. The left-hand one was taken with the specimen mounted on the spectrometer in position (*a*) and the right-hand one in position (*b*). The black semi-circular dots on the left of each photograph are the centre spots and the figures written beside them are the setting angles. The setting angle when the specimen was parallel to the incident beam was 172°5' in each set. The reflected spots are seen on the right; the darker series are due to K $\alpha$  radiation for which the reflecting angle is 24°3', and the fainter series to K $\beta$  radiation.

It will be seen that in position (*a*) the spots are small but the range of angles over which reflection takes place extends over 10 or 12°. On the other hand in position (*b*) the spots are elongated into appreciable arcs of Debye rings, and the range of setting angles at which reflection occurs is limited to 2° from 196° to 198°. It will be noticed also that the spot of maximum intensity is at 197°. On one side of this maximum the reflections only extend through a range of 2° to 195°. On the other side, however, there was still a visible spot after 8 minutes' exposure at 206°.

These photographs prove that all the parts of the material which have rotated through angles greater than 2° have rotated about the transverse

<sup>2</sup> "Distortion of Crystals of Aluminium under Compression," *Proc. Roy. Soc., A* 111 529.

direction in the plane of slip. Some of them have rotated as much as  $90^\circ$  about this direction, and moreover in all cases the direction of rotation is the same. This direction of rotation is in fact the same as that which might be expected if the detached portions of the crystal acted as rollers between the slip planes, but it is very much less than would be necessary if they actually played the part of rollers.

### Rotation of Material in Neighbourhood of Regions of Concentration of Stress.

If the slipping of one crystal plane on another does not take place simultaneously over the whole of the section of the specimen by a plane of slip, then at the ends of a region of slipping there will be a concentration of stress. The displacements of the material above and below this region relieve the stress in the middle and concentrate it at the ends. If the material is considered as elastic except in so far as it has slipped over a limited area of the slip plane, the displacements and stresses are those round a limited crack in a material when a shearing stress is applied parallel to its plane. Considering a crack as the limiting case of a very long ellipse, these can be calculated using the theory of elasticity.

I have worked this out with the following results :—

(1) The stress concentrates at the ends of the crack, and the direction of maximum shear stress in the region where it is greatest is that of the crack itself—so that it would tend to extend in the same direction.

(2) Throughout the whole of the two regions of stress concentration, *i.e.*, at the two ends of the crack, the material is rotated about the transverse direction and the direction of rotation is everywhere the same, namely that in which rollers in the crack would rotate if they rubbed on the top and bottom of the crack. There is a concentration of rotation in the regions of concentration of stress.

The rotation of an elastic material at the ends of a limited crack or area of slipping is therefore exactly what is observed by means of X-rays in a strained single crystal.

Returning now to the load-extension curve. The load at which slipping takes place will depend, according to this theory, on the ratio in which the maximum stress is increased above the applied stress. This depends as was pointed out by Inglis and by Griffith on the curvature of the end of the crack and on its length. The curvature at the end of the crack may be taken as depending on the atomic structure and therefore independent of its length. At the point of greatest concentration the stress is increased, as in Griffith's case, in a ratio which is proportional to the square root of the length of the crack. Considered as a two-dimensional system the stress is, as it were, drained out of an area proportional to the square of the length of the crack, or region of slipping. In the early stages when slip has occurred in a few places only, the ends of a crack can concentrate stress from a large region; consequently the ratio of the maximum stress to the applied stress is large, and a small stress applied to the specimen will raise the stress at the point where it is greatest to the value necessary for slipping.

As the slipping proceeds on more and more planes the undisturbed parts from which stress can be drained into regions of stress concentration become smaller and smaller, so that effectively (*i.e.*, from the point of view of stress concentration) the newly-formed cracks are smaller and smaller. The ratio in which stress is increased therefore decreases, and the stress

which must be applied to the specimen in order that slipping may occur at a point of stress concentration therefore rises.

It appears therefore that a theory of this kind can be made, qualitatively at any rate, to account for the rapid rise in the load-extension curve at small values of the extension.

Turning now to the energy absorbed in the material, according to this theory it would be in the form of strain energy in the regions of stress concentration. Using the value appropriate to a crack in an elastic medium under shear stress parallel to the direction of the crack, I find that if during the formation of a small strain  $\delta s$   $n\delta s$  cracks are formed, each of length  $zc$ , then the ratio of energy retained in the material to energy dissipated in the form of heat is constant if  $nc^2$  is constant. If one makes the assumption that the length of a new crack formed in a piece of previously uncracked material is proportional to the linear dimensions of this piece, then  $nc^2$  would be constant, and the observed constancy of the ratio of energy absorbed to heat dissipated would be explained.

### Conclusion.

It seems that a consistent theory might be formed on the assumption that the resistance to shear parallel to a crystal plane of slip is not small, and that much greater concentrations of stress can occur in an unbroken crystal than in one which is already filled with regions of stress concentration. The alternative theory that the resistance to shear is weak in a single crystal and that it is strengthened by the formation of imperfections which prevent rows of atoms from slipping seems untenable in the case of metals like aluminium, though it may be applicable to metals like zinc for which there are fewer possible crystallographically similar modes of slipping.

## HYSERESIS IN RELATION TO COHESION AND FATIGUE.

By B. P. HAIGH, ROYAL NAVAL COLLEGE, GREENWICH.

*Received 8th October, 1927.*

Just two hundred and fifty years have passed since Robert Hooke—in the words “*Ut Tensio sic Vis*”—gave the solution of the anagram that a year earlier he had enunciated as the law of elasticity. To-day, Hooke’s law stands foremost among the experimental laws of cohesion, and is accepted as an adequate basis for the mathematical science of Elasticity. This general acceptance is now associated, however, with a growing recognition of the approximate character of the law—which, in metals, is seldom fulfilled within the limits of observation in careful experiment. The discrepancies observed in different metals deserve attention less for their practical importance—which is often only slight—than because they may afford some clue to the physical nature of cohesion and fatigue.

The two chief types of discrepancy observed in “static” tests, e.g. in tensile tests on pieces fitted with sensitive extensometers, may be described as follows: (1) Metals are not perfectly elastic in the sense that testpieces do not return to datum length at datum load, even when the loads applied are only moderate. Although glasses and other cold vitreous substances

are almost perfectly elastic, and some metals nearly so, other metals—and notably slowly annealed samples with coarse crystalline structures—show large “permanent” strains on their first loadings. It is understood that recent work on single crystals of aluminium<sup>1</sup> has shown that these crystals exhibit little or no elasticity in their virgin state but behave in a plastic manner. From such considerations it is inferred that elasticity is an acquired rather than an inherent property of the crystalline structures found in metals. (2) In cyclic loading after the metal has acquired some measure of elasticity—*i.e.*, when little if any permanent strain is produced in successive cycles—the load-extension graphs for loading and unloading diverge perceptibly, forming a loop whose area represents the work done on the piece during the cycle of load. It is inferred that the elasticity acquired by metals is not accurately described by Hooke’s law, but is associated with “hysteresis.”

Hysteresis was probably first investigated by Lord Kelvin in experiments carried out in the University of Glasgow. Dr. Muir established many of the more important features of the phenomena, in experiments described in Ewing’s “Strength of Materials;” and in recent years, the study of hysteresis in static tests has been facilitated by the photographic extensometer invented by Professor Dalby. The area of the hysteresis loop increases rapidly with increase in the range of stress, but diminishes during successive cycles with a given range of load—at least in many examples.

An objection to the use of the word “hysteresis” in this application may be raised on the ground that it signifies—etymologically—“lagging behind with respect to time;” whereas, actually, investigation shows that speed of loading has little if any influence on the form or area of the hysteresis loop. Hopkinson and Trevor-Williams<sup>2</sup> and Rowett<sup>3</sup> carried out tests with widely different frequencies and found the work absorbed per cycle nearly the same. It does not appear that the action is comparable with the viscous flow that occurs in warm vitreous substances.

What becomes of the work done during cyclic loading? A quantity of heat is generated in the testpiece, tending to raise the temperature until conduction and convection carry it away. Whereas the work done per cycle is known as the “mechanical” hysteresis, the heat generated per cycle is known as the “thermal.” There is no *prima facie* reason to assume that mechanical and thermal hysteresis are necessarily equivalent in value: Physical changes in the inelastic metal might account for a difference; but Hopkinson, Trevor-Williams, and Rowett conclude that any difference between the two must be slight in the steels that they used.

In their experiments on thermal hysteresis, Hopkinson and Trevor-Williams used a thermocouple to measure the temperature gradient in the metal. The rate at which heat is liberated can then be deduced in a simple manner in terms of the known conductivity of the metal. Although some heat is always convected away from the exposed surface of the testpiece, the greater part is conducted along the testpiece to its ends. In experiments that the present author—with the valued assistance of his colleague Mr. T. S. Robertson, B.Sc.—has carried out during the past few years, this method has been developed in such a manner as to eliminate certain experimental difficulties.

Fig. 1 illustrates the form of testpiece and the arrangement of thermocouples used in the experiments now to be described. The testpiece,

<sup>1</sup> Taylor and Elam; and Gough, Hanson, and Wright, *Proc. Roy. Soc.*, 102, and 226.

<sup>2</sup> Hopkinson and Trevor-Williams, *ibid.*, 87.

<sup>3</sup> Rowett, *ibid.*, 89.

formed with cylindrical mid-length, larger screwed ends and long transition curves, is loaded in pull and push in an electro-magnetic fatigue testing machine of the well-known type designed by the author.<sup>4</sup> The machine applies a cyclic load that varies between equal or unequal values of pull and push, and measures the range of load and also the mean load in the cycle. The load varies in a close approximation to a sine wave, and the

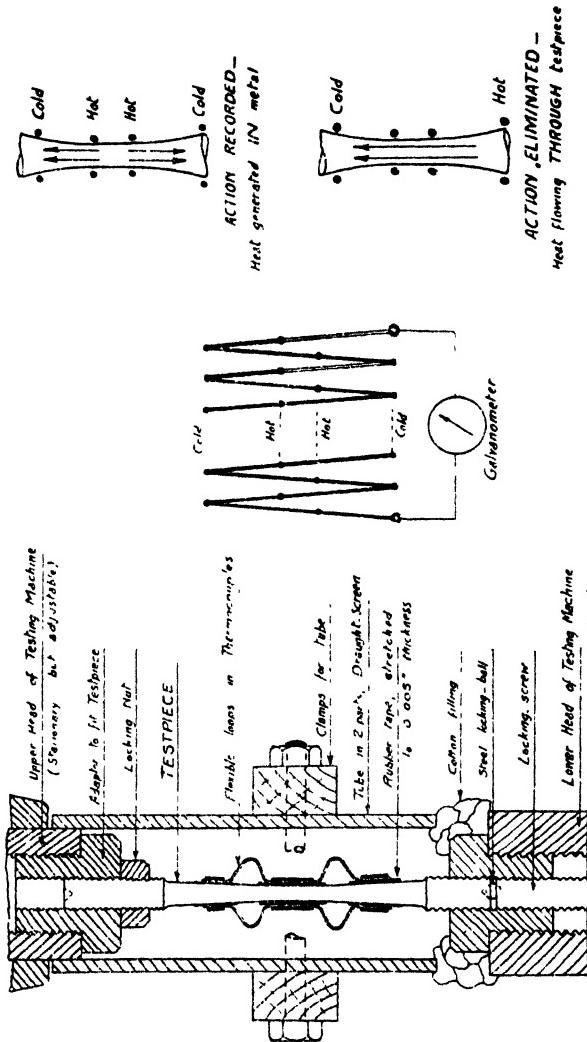


Fig. 1.—Testpiece and thermocouples used in hysteresis tests.

frequency used in all the tests described was 2000 cycles per minute. In the tests described, the load was adjusted to vary between equal values of pull and push. This type of machine offers special advantages for the purpose, in respect that the whole volume of the cylindrical mid-length of the testpiece is subject to the same known range of stress. Also, since the testpiece stands stationary and in an accessible position in the machine, thermocouples or other attachments can be fitted with ease.

The arrangement of the thermocouples was devised with the dual object as follows: (1) to measure the temperature gradient that corresponds to the flow of the heat generated in the cylindrical mid-length of the test-piece, and (2) to eliminate the effect of any other temperature gradient, such as may exist if one end of the testpiece is warmer than the other. Forty junctions are arranged in four groups, two near the centre of the piece and two further away. The junctions are made by electrically welding the ends of the short wires and are connected in series. In order to introduce some degree of flexibility, the wires are bent and are bedded and tied to the testpiece by stretched rubber tape. The circuit is led to a galvanometer of suitable sensitivity or to a Cambridge recorder—which latter type of instrument keeps a continuous record during long fatigue tests lasting several days and nights.

The use of such a thermometric device affords a welcome addition to the ordinary fatigue test in which, as a rule, only the range of stress and the number of cycles required to cause fracture are recorded. The application of the device is analogous to that of the clinical thermometer in medical practice, giving a symptomatic indication of the progress of the case. It is found that hysteresis varies widely and in strikingly different ways in different metals and in tests with different ranges of stress. In the

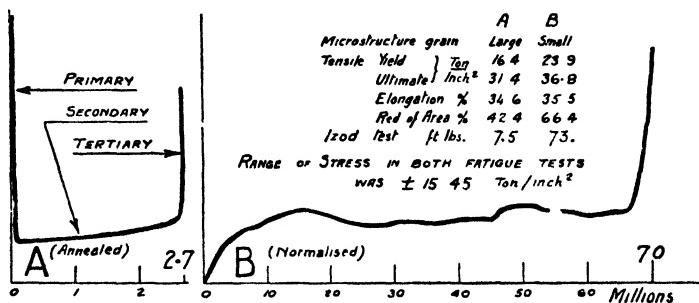


FIG. 2.—Results for carbon-steel with different heat-treatments.

diagrams that follow, the ordinates represent the readings of the galvanometer—proportional to the temperature gradient and, therefore, to the rate at which heat is being liberated from the testpiece. The abscissæ give the numbers of load cycles applied during the course of the test; and as the frequency of loading is constant, this corresponds to a time base.

Fig. 2—which includes two graphs, A and B—has been chosen to illustrate a contrast that is typical of the results obtained in the whole wide field of investigation, which includes tests on several hundred pieces. In all cases, the results are comparable with one or other of these graphs or are intermediate between them.

Graphs A and B were obtained in tests on two samples of the same carbon steel with different heat treatments. Whereas sample A was close annealed—heated to 975° C. in a closed box and allowed to cool slowly in the furnace,—sample B was normalised—heated to 850° C. during a total time of about 1½ hours, and allowed to cool on the floor of the shop. This choice of heat-treatment was originally chosen in order to illustrate the influence on the Izod notched-bar test: Whereas the annealed metal had a coarse-grained structure and gave only 7.5 ft.-lb. mean Izod figure, the normalised samples were fine-grained and gave 73 ft.-lb. Izod. But for the object of the present tests, the influence of heat-treatment on the yield

point is more important: Whereas the yield point is only  $16\cdot4$  Ton/inch $^2$  in the annealed sample, it is much higher at  $23\cdot9$  in the normalised. The two fatigue tests illustrated were carried out with the same range of stress, *viz.*  $\pm 15\cdot45$  Ton/inch $^2$ ; and the A and B pieces broke after  $2\cdot75$  and  $70$  million cycles respectively. Although these endurances are widely different, both are fairly long; and it is probable that the fatigue limits of the two samples are nearly alike and in the region of  $15$  Ton/inch $^2$ . The A metal therefore may be regarded as typical of many in which the fatigue limit approaches the yield point of the metal and exceeds whatever value might be reported as the elastic limit revealed by an extensometer test. The B metal, on the other hand, may be regarded as typical of others in which the fatigue limit lies well below the yield point, and even below the elastic limit value for a test of ordinary and not too critical character.

Inspection of the A graph, which is typical of the results obtained with annealed ductile metals, reveals three characteristic stages in the course of the fatigue test. For convenience, these are henceforward described as the PRIMARY, SECONDARY, and TERTIARY stages of the test. The B graph differs from the A in two respects, *viz.*, there is no primary stage at the start of the test; and the secondary stage develops gradually, hysteresis starting at a

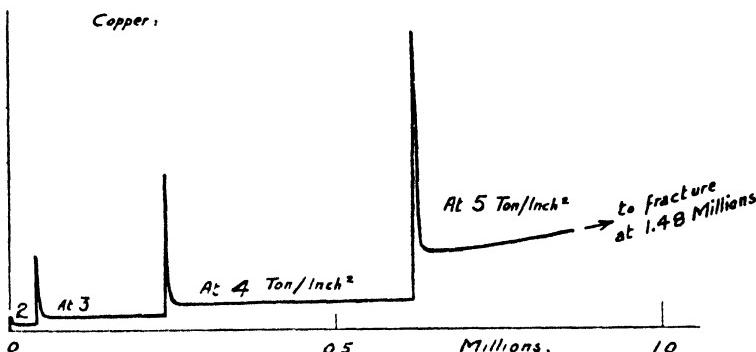


FIG. 3.—Primary and secondary stages in copper.

low value and rising gradually to a higher, at which—in this instance—it continues more or less constant or rises somewhat during a very long time before eventually the brief tertiary stage leads to fracture. It is proposed to consider the three stages separately and in the sequence Primary, Tertiary, Secondary—the last-named being regarded by the author as the characteristic feature of fatigue.

The PRIMARY stage manifests itself in annealed metals as a brief evolution of heat at the beginning of the fatigue test. It seldom continues for more than 250,000 cycles when the range of stress is maintained constant; but if the range is increased at intervals as in the manner indicated in Fig. 3, a fresh primary stage follows each increase and gradually dies away—leaving only the secondary action. Although the primary stage is only brief in comparison with the total endurance of the testpiece in a long fatigue test, it is long in comparison with the numbers of cycles that are commonly imposed in "static" observations of hysteresis. It follows therefore that the observations taken in such static tests relate wholly to the primary action when that is present, and to the secondary when the primary is absent. It follows that a conclusion drawn by Rowett from his static tests on hard-drawn and annealed steel tubes tested in torsion—that hysteresis is

more evident in annealed steel—may require limitation. Whereas hysteresis of the primary type is indeed more evident in annealed metal, hysteresis of the secondary type attains nearly the same value in the two samples compared, in Fig. 3, with the same range of stress.

Repetition of stress in the primary stage "hardens" the metal, rendering it more nearly elastic; and as the fatigue test proceeds during the first quarter million cycles, the "elastic limit" and Brinell hardness gradually rise in value. Microscopical examination reveals the formation of slip-bands<sup>5</sup> in precisely the same way as in tests with static loads;<sup>6</sup> and there appears no reason to doubt that the hysteretic action in the primary stage is due to plastic slip of precisely the same nature as is observed in tensile and other tests of ductility and in processes such as wire-drawing.

The manifestation of the primary stage appears to depend wholly on the relation between the range of stress adopted in the fatigue test and the value of the elastic limit or of the yield point of the ductile metal. As is now well known, the fatigue limit of a ductile metal bears little if any direct relation to the nominal elastic limit, and may be much higher or much lower in different samples. If the fatigue limit is lower and is determined by experiments with low ranges of stress, no plastic flow or primary stage will be observed in the tests. But if the fatigue limit is higher, so that its value can be ascertained only by using ranges of stress that exceed the elastic limit, the phenomena of plastic flow naturally make themselves evident during the tests.

According to this view, the phenomena of the primary stage afford no reliable indication of what the fatigue limit may be, but are associated wholly with plastic flow. It would be hard indeed to accept the contrary view—that such transient phenomena, so intimately related to the elastic limit and so often absent when this is high—can afford any indication of whether the metal will break long after the primary stage has apparently ceased. Even when the primary action is manifested under the ranges of stress that produce fatigue, it shows no marked change in magnitude or nature when the range attains the limiting value. For these reasons it appears that "five minute" tests, such as recently have attracted considerable attention, cannot except in specially restricted fields of application serve to reveal the fatigue limit in a reliable manner.

Primary hysteresis or plastic flow, far from being a source or symptom of danger of fatigue, is probably quite the reverse in respect that the associated slipping not only hardens the metal but may often discount the dangerous influence of notches and other discontinuities of section. In more elastic metals, such discontinuities may produce local concentrations of stress approximating to those indicated by mathematical or optical analysis, and may so cause premature fatigue and fracture. This aspect of the influence of plastic flow was investigated some time ago by Wilson, Beale, and the present author,<sup>7</sup> who showed that the dangerous influence of discontinuities in flat plates subject to pulsating tension was much less in mild steel than in harder—working with the same "factors of safety;" and in any case less than indicated by mathematical analysis.

The TERTIARY stage of fatigue—which follows the long-continued secondary and immediately precedes fracture—is usually only brief but may extend over several million cycles. Hysteresis rises gradually, slowly at first but with increasing rapidity until the testpiece breaks. The action is

<sup>5</sup> Ewing and Humphrey, *Phil. Trans., A.* 200.

<sup>6</sup> Ewing and Rosenhain, *Proc. Roy. Soc., 65*.

<sup>7</sup> Wilson and Haigh, and Haigh and Beale, *Brit. Assoc., 1922-3-4.*

attributed to the plastic flow associated with the gradual opening of the crack which is often visible during the later part of the tertiary stage although never during the secondary. It appears that the duration of the tertiary stage may be longer in large pieces than in smaller, as if the rate of propagation of the crack might be independent of the size of the testpiece; but so far as the author is aware, this action has not received the attention that it deserves in view of its practical importance.

The action during the tertiary stage is regarded by the author as of only minor theoretical interest from the point of view of its bearing on fatigue. The action in the final rupture is nearly the same as in a notched bar tested under steady or impactive tension. In this connection it is desirable here briefly to refer to certain deductions that may be drawn from comparisons between the forms of fracture obtained with different kinds of loading, steady, pulsating or alternating. Four years ago<sup>8</sup> the author showed that two distinct modes of fracture could be distinguished in combination in all cases; and that the "cupped" form of the ordinary tensile fracture of a ductile metal was determined in large measure by the influence of "triple-tensile" stress (tension acting in three directions) in the core of the testpiece. While the marginal cup fails by slipping under the shear component of the applied tension, the core fails in quite a different manner—by cracking in a brittle manner under the action of triple tension induced as a consequence of the necking associated with the reduction of cross-sectional area. When the occurrence of triple-tension is prevented, e.g., as in wire-drawing, by the application of the lateral pressure of the dies, plastic flow continues much further than in a tensile test because it is not then interrupted by the cracking of the core. The fatigue fracture of a ductile metal also comprises two distinct parts that can be attributed to different physical actions. The first part, often discoloured in a remarkable manner and always of a brittle character—free from plastic disturbance—is regarded as the characteristic feature of the fatigue crack. The second part, which completes the fracture and is evidently associated with slipping of the nature of plastic flow, may be regarded as no more than the subsequent tearing of the ductile residuum, comparable with the later stage of the fracture of a notched bar.

It would be well if the scientific use of the word fatigue were restricted to describe the action that causes the brittle fracture under moderate loads, but the word is often and unfortunately used more widely. If the range of stress on a testpiece is high enough, slip is inevitable in any ductile metal; and if the mean stress in the cycle is not zero, the testpiece will extend or compress as in a tensile or compression test, according as the mean stress acts as pull or as push. When a piece is extended and broken in this manner under a heavy pulsating tension applied for only a moderate number of cycles, the load required—and the elongation, reduction of area and form of fracture—are nearly the same as in an ordinary tensile test with steadily increasing load. But such a fracture, although produced by pulsating stress, can hardly be regarded as caused by fatigue. The real and as yet still unsolved problem of fatigue is to ascertain how the character of the metal changes during the long-continued fatigue test, so that the tertiary stage begins and the crack starts to open in a brittle manner under such moderate ranges of stress as are required in fatigue tests. At the fatigue limit, the semi-range of stress is seldom as much as 60 per cent. of the ultimate tensile strength, and is often as low as 30 per cent. even in metals with "clean" microstructures free from openings or inclusions of foreign matter.

<sup>8</sup> Haigh, Brit. Assoc., 1923.

The SECONDARY stage of a fatigue test—which continues through the greater part of the life of the testpiece—is characterised by the relatively slow rate of variation of hysteresis. The value may rise or fall slowly or may remain constant for long periods in tests carried out with constant range of stress. The secondary stage is masked only when the range of stress is so high and the endurance so brief that the tertiary stage commences before plastic strain has ceased. The secondary action is observed in all metals, even under small ranges of stress, and is often described as “elastic hysteresis.” The phenomena of the secondary stage differ appreciably in different cases; and it appears that the action deserves careful study for two reasons. Firstly, it appears to be inherent to the state of elasticity induced in metals by the treatments that render them “elastic;” and secondly, it appears to be at least a possible cause of fatigue.

The hysteretic actions of the primary and secondary stages do not seem to be related in any quantitative manner: large primary hysteresis is often associated with small secondary or *vice versa*. The contrast between graphs A and B in Fig. 2, illustrates a typical instance—the treatment that has completely changed the incidence of the primary action has left the secondary action nearly unchanged, in this example. There is no reason to assume that the secondary action is merely a residuum of the primary. On the contrary, the two actions appear to be distinctly different although, doubtless, they may have something in common.

The work done on the metal in the secondary stage is, as in the primary, at least very nearly equivalent to the heat liberated. When a testpiece is removed from the fatigue machine and tested “statically” with an extensometer, the area of the hysteresis loop obtained closely corresponds to the gradient of temperature observed in the fatigue test. Since the total quantity of heat liberated in the course of a long-continued secondary stage is very great—commonly of the order that would suffice to melt a steel testpiece—no relation other than equivalence could be expected from such a comparison.

The great magnitude of the quantities of work and heat involved in the secondary action lend added weight to two considerations that lead to the conclusion that the primary and secondary actions must be essentially different in character. Firstly:—Although the plastic flow during the brief primary stage appreciably hardens the metals in which it is observed, and although all ductile metals are hardened in similar manner when work is done upon them in tests or operations that involve plastic flow, it does not appear that the much greater quantities of work that are often done on the same metals during the course of the secondary stages of fatigue tests cause any corresponding change in hardness. If tensile or Brinell tests are carried out on identical testpieces that have been tested to earlier or later points in the secondary stage, no perceptible difference is found in the results. And secondly:—Although slip-bands form plentifully during the brief primary stage, few if any form during the long-continued secondary stage during which so much more work is done on the metal. If the bands formed during the primary stage are erased, fresh bands are seldom observed to form during the secondary; and even when some few may be observed, they afford no sufficient quantitative explanation of the great quantity of work absorbed.

For these reasons it is held to be established that the “elastic hysteresis” observed during the secondary stage of a fatigue test is fundamentally distinct from the plastic flow observed in the primary stage and in other tests and operations involving ductile displacement. It remains now to be considered whether elastic hysteresis is related to fatigue.

When plastic flow is slight or absent in a fatigue test, elastic hysteresis is often observed to increase gradually during the repetition of great numbers of cycles. In graph B—Fig. 2—for example, at least 10 million cycles were required to raise the value gradually to a quantity that remained nearly steady or rose somewhat during the 60 million cycles that preceded the tertiary stage. It is inferred that the conditions requisite for the action are not always fully established in the metal at the beginning of the test, and that parts of the metal are initially in a state that is unstable under the conditions of the test.

It is probable that the variations of elastic hysteresis shown in the wavy profile of the secondary portion of the graph B—Fig. 2—originate only from small variations in the range of stress applied during this long test. For the purpose of eliminating such variations in the range of stress, Mr. Robertson has devised a control circuit for use in conjunction with the

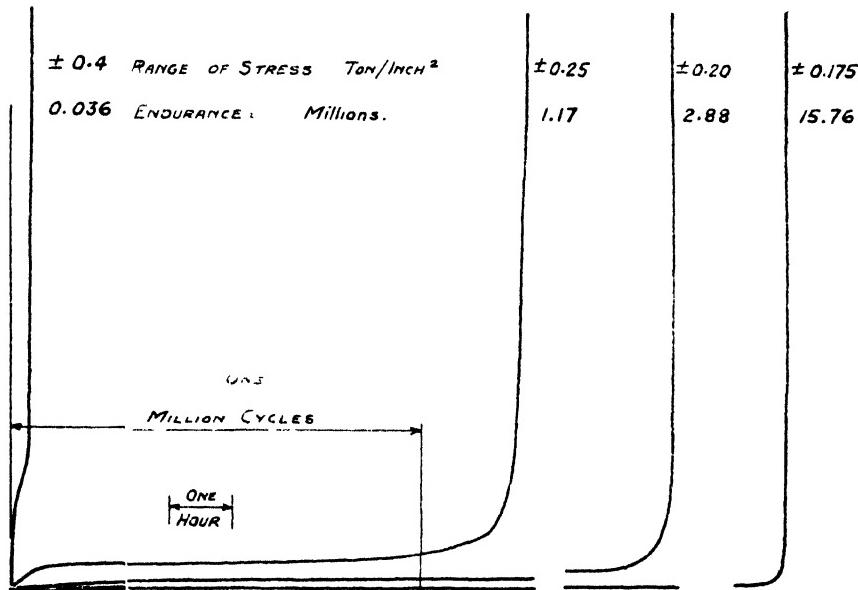


FIG. 4.—Secondary and tertiary stages in lead.

electro-magnetic fatigue testing machine employed. In this circuit, a 3-electrode valve actuates a low-resistance shunt regulator by means of a relay and clockwork; and the device appears to be sensitive, convenient, and reliable for long periods. Fig. 4 illustrates a group of tests controlled in this manner. After the initial rise, secondary hysteresis continues to rise very slowly and steadily at different rates with different ranges of stress. In the tertiary stages, hysteresis attains the same value with different ranges, but the manner of rise appears to vary with the range of stress. As will be mentioned again later, the tests illustrated in this diagram were carried out on lead of high purity. But as a general rule for tests that eventually lead to fracture, elastic hysteresis continues to rise during the greater part of the secondary stage of the test. It is inferred that elastic hysteresis is associated with or at least reflects the progress of fatigue in the testpiece.

In a wide variety of metals, the initial rise of elastic hysteresis occurs in the manner represented in Fig. 5 and becomes evident only when the range

of applied stress exceeds an ascertainable value. In this particular tempered nickel-chrome steel, only slight secondary hysteresis—without primary—was observed in brief preliminary tests at  $\pm 20$ ,  $\pm 21$ ,  $\pm 22$  and  $\pm 22\frac{1}{2}$  Ton/inch<sup>2</sup>. At the last mentioned range, however, the value was seen to be rising slowly, even in the brief test. When the range was increased to  $\pm 23$  Ton/inch<sup>2</sup>, hysteresis rose promptly and continued to rise rapidly. The rate of increase decreased for some time and finally rose again in the tertiary stage. The piece broke after 0·552 million cycles at  $\pm 23$  Ton/inch<sup>2</sup>, and it is probable that it would have broken at  $22\frac{1}{2}$  with somewhat longer endurance. In many metals, likewise, the initial rate of increase affords a convenient index of the probable approximate value of the fatigue limit.

It is only rarely that a testpiece escapes fracture if elastic hysteresis has continued to rise for any considerable period, but the period required to form a reliable opinion of whether the value is continuously rising may be very considerable. In some instances, hysteresis has been observed to increase slowly during several million cycles and to attain a maximum followed

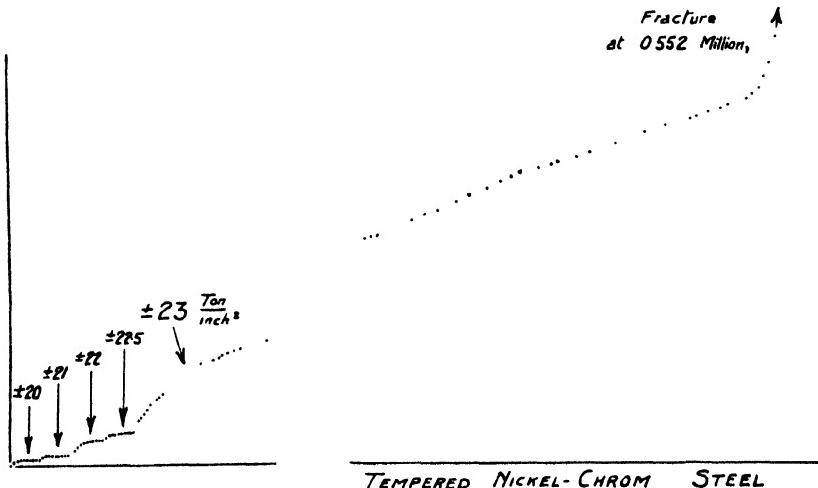


FIG. 5.—Rise of secondary hysteresis in nickel-chrom steel.

by a gradual decrease that continued for 30 million cycles without fracture. This type of variation is recorded only when the range of stress lies near the accepted fatigue limit of the material; and the contrast between the long rising graphs leading to further rise and fracture, or to gradual fall without fracture, appears to indicate a very close relation between elastic hysteresis and fatigue. Alternatively, if such a relation be assumed to exist, the contrast between the two types appears to afford welcome evidence that metals really possess fatigue limits below which repetition of stress leads to no accumulation of change, and is "safe."

It may not always be valid to assume that no long-continued decrease in hysteresis will be followed by fracture. In a certain ductile brass, for example, hysteresis decreased continuously during 5 million cycles although the piece fractured after 14·02 millions at 7 Ton/inch<sup>2</sup>. And even at  $7\frac{1}{2}$  Ton/inch<sup>2</sup>, decrease continued for nearly a million cycles and the piece fractured at 2·80 millions. But in this metal, slipping was evident during the periods of decrease, and the action is attributed to abnormally delayed

plastic slip in a lengthy primary stage. The approximate fatigue limit of  $7 \text{ Ton/inch}^2$  corresponds to only 30 per cent. of the ultimate tensile strength; and is well within the plastic zone. The hysteresis of the primary stage showed no rapid diminution, but tailed off gradually into the secondary stage. Even in this special case, however, hysteresis increased in the usual manner during the later courses of both tests; and it may be that such exceptional cases also prove the rule that continuously decreasing or constant elastic hysteresis never leads to fracture.

Many hundreds of pieces have been studied in the manner described,

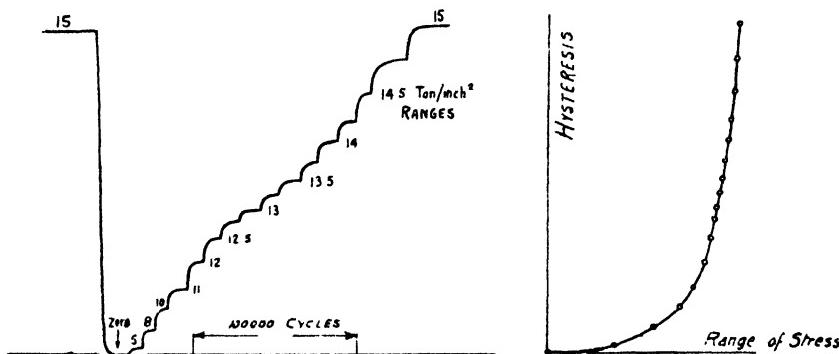


FIG. 6.—Relation between elastic hysteresis and range of stress.

and it is considered that the intimate relation between elastic hysteresis and fatigue is established.

In order to ascertain how elastic hysteresis varies with the range of stress applied, in testpieces that have reached different stages in the course of fatigue tests, many long tests with constant ranges of stress have been interrupted so that observations could be taken with smaller ranges of stress. Fig. 6 represents a typical experimental record taken during such an interruption, and shows how the thermocouples quickly respond to any variation of conditions. The time lag of the device is only slight; and as the wires are bedded on a very thin film of stretched rubber, it is probable that the device can be regarded as reliable for the object in view. In this connection, it may be mentioned that variations in the thickness of the rubber, within limits, make only a slight difference in the values recorded. Fig. 6 represents also the relation between the elastic hysteresis and the range of stress. It appears that hysteresis varies with no constant power of the range, and that the index increases with the range to values that usually lie between 3 and 4. The forms of the graphs suggest that elastic hysteresis must continue even at the lowest stress-ranges. When hysteresis is increasing during the continuance of a fatigue test carried out with a range of stress greater than the fatigue limit, the relation between the two values plotted in such graphs changes in an interesting manner during the course of the test; but still further work in this direction is required before any general conclusions can be drawn. When the range applied in the long test lies below the fatigue limit, the form of the hysteresis-range graph often remains unchanged for long periods up to 50 million cycles.

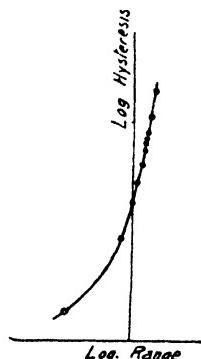


FIG. 6(a).

The relation between elastic hysteresis and range shows conclusively that elastic hysteresis cannot be regarded as a direct measure of the rate at which fatigue is or is not being effected in the metal. It can be regarded only as a symptom of an action that may or may not, in different circumstances, eventually lead to fatigue.

It is probably generally known that fatigue fractures may be either inter- or intra-crystalline. In this connection it is interesting to note that the course of the action, so far as it is revealed by the changes of elastic hysteresis, is precisely the same in the two cases. The graphs given in Fig. 4 for example, for lead of a high degree of purity, were for pieces that broke in a definitely inter-crystalline manner. Similar graphs are obtained for lead-alloys, and alloys and metals of widely different kinds—many of which break in the more common intra-crystalline manner. It is inferred that whatever may happen on the crystal boundaries in the one case, causing elastic hysteresis and often leading to fatigue, happens in a very similar manner in other cases on surfaces within the grains—presumably on surfaces that have suffered slip in consequence of the processes of manufacture, or have slipped during the plastic flow of the primary stage. The gradual rise of elastic hysteresis during the earlier part of the secondary stage is regarded as evidence that such surfaces do not remain in any stable condition under the variations of stress.

When metals are exposed to the actions of corrosive reagents, applied to their surfaces during the continuance of fatigue tests, the endurance and fatigue limit are appreciably reduced;<sup>9</sup> and it has been shown that the action is not merely due to pitting, but to the combined action of the two sources of energy—chemical and mechanical.<sup>9</sup> It appears inconceivable that the corrosive reagent acts as a lubricant on finite surfaces, facilitating slip; and in the author's view of the general problem of fatigue, the chemical reagent probably attacks atoms involved in the action that we call "elastic hysteresis," rendering the action non-cyclic by chemical combination where, in the absence of the corrosive reagent, it might have been cyclic.

Is it possible to formulate any brief description of the probable physical nature of elastic hysteresis? To do so, it appears to the author necessary to rely on a "dynamic" rather than on a "static" conception of stability in metallic structure, and to take account of the thermal motions of the atoms or molecules. The difference between the crystalline and the amorphous states may then be described as the difference between a regular motion and a more violent and irregular motion of the same component atoms, although this use of the word irregular doubtless requires qualification. Between any crystalline mass and any amorphous mass that are nominally in contact, there must exist a layer in which the state of motion is intermediate—changing gradually from the regular to the irregular type. It is to the hypothetically finite thickness of such layers, on the crystal boundaries and on slip-planes and elsewhere, that the author would attribute the extended hardening influence of the boundaries and slip-planes; and it is within such layers that the action of elastic hysteresis is conceived to occur. When applied forces do work on the metal, in the loading stage of a cycle, the atoms are not merely displaced but are given additional energies of motion; and some that moved in more regular ways will now move in less regular. When the forces are reduced in the unloading stage of the cycle, the additional energy of motion is only partly returned as work because the

<sup>9</sup> Haigh, *Inst. of Metals*, 1917.

disturbed atoms—in settling down from the irregular to the regular motion—give impacts that generate vibrations or “heat.” Thus the cyclic changes in the intermediate layers are irreversible in the thermodynamic sense, even when—under moderate ranges of stress—the atoms return to their original positions and states of motion.

It is more difficult to describe the limiting condition that defines fatigue, and it is probable that no single description covers all cases. When the range of stress is increased, the intermediate layers doubtless thicken to include greater numbers of atoms, and the numbers simultaneously involved may be so great that orderly replacement is no longer attained. In the thicker mass, some of the atoms may succeed in settling down permanently from the metastable irregular state of motion to the more regular state, although such a change is hypothetically impossible in the thinner layers that exist under lower ranges of stress or in the unstrained metal. Such a change may be described as crystallisation, and would be accompanied by a contraction of volume with liberation of heat. The result of such a contraction may be pictured to be the same as in an ingot whose interior cools after the exterior has become unduly rigid. Triple-tensile stress—which, Mr. Stromeyer suggests, might be called “clink stress”—would produce internal “clinks” in the form of cracks through the zones of contraction. In different metals, however, with different metastable structures, and in different circumstances of corrosion and temperature, different interatomic actions may occur in the intermediate layers pictured as the seat of elastic hysteresis, and these may produce contraction and triple tensile stress in different ways.

According to the views advanced above, “elastic hysteresis” should no longer be regarded as an incidental imperfection of a more ideal state of elasticity represented by Hooke’s law, but rather as an inherent characteristic of the state of elasticity that can be acquired by metals; and that state of elasticity should be attributed to the influence of the grain boundaries and surfaces of slip within the grains, rather than to the crystalline metal. Elastic hysteresis is regarded as a process that is thermodynamically irreversible even when it occurs in a manner that is perfectly cyclic; and of a nature totally distinct from plastic flow or slip. It is regarded as the action that leads to fatigue when it occurs in a manner that is only imperfectly cyclic; and fatigue fracture is attributed to the action of triple-tensile stress induced by local contractions of volume.

## NOTE ON SOME FATIGUE PHENOMENA WITH SPECIAL RELATION TO COHESION PROBLEMS.

By H. J. GOUGH.

*Received 7th November, 1927.*

For the purposes of the present note, fatigue phenomena will be understood to be the characteristics exhibited by metals when subjected to cyclical variations of stress or strain. The practical importance of the subject of fatigue needs no emphasis. Very few of the more important machines or structures can be designed without some consideration being given to the fatigue-resisting strengths of some of their components. Neither can it be denied that the majority of the more complex failures of such machines or

structures can be directly traced to fatigue. From the theoretical viewpoint, also, fatigue failure presents many features of peculiar interest. For example, by a suitable choice of the applied stressing system, it is possible to produce a fracture of a "brittle" appearance in the most ductile metals, not only when these metals are in the usual finely-divided crystalline state, but also when they are in the form of a "single" crystal. It must not be assumed that failure under fatigue is not, in some cases, accompanied by considerable mass distortion; fatigue failures can be produced in specimens of the same metal such that the total distortion of the specimen, as a whole, can be made to vary from practically zero to a maximum, merely by altering the type of the applied stress system. Again, the cycle of applied stress can be so adjusted that it will produce complete rupture of the metal only after a very great number of repetitions of the cycle, thus affording opportunities for examining various characteristics of the progressive break-down of cohesion at many stages prior to final rupture. It is not, therefore, surprising to find that fatigue problems have attracted considerable attention during recent years. A large number of experimental investigations have been made and considerable test data have been obtained. In spite of this, the present theoretical position is very uncertain and no fundamental theory of fatigue has yet been published. Nor is it *likely* that any of the "theories"—based on experimental observations alone—can possibly be complete; for fatigue appears to be controlled by three main circumstances, namely, the stress system applied, the temperature at which the test is conducted and the nature of the surrounding medium. Fatigue testing at elevated temperatures is only now beginning to receive attention, while, although ten years have elapsed since Haigh<sup>1</sup> first drew attention to the accelerated effects of fatigue when a corrosive agent is present, it was not until 1926 that McAdam<sup>2</sup> published the first real quantitative study of corrosion-fatigue. Hence, considerable doubt must arise before the general application is admitted of any theory that results from an experimental study of fatigue phenomena occurring under ordinary air conditions of temperatures and surrounding medium. All existing theories fall into this class.

There are certain aspects of fatigue phenomena which appear to afford especially promising lines of experimental investigation with regard to the main problem of the progressive breakdown of the cohesion of metals. Among these are (1) cyclical stress-strain relations, (2) the nature of deformation by plastic strain (slip), (3) the hardening produced by slip, and (4) the manner of the initiation and propagation of fatigue cracks. In the present note, it is proposed to offer a brief summary of some of the recent researches, conducted at the National Physical Laboratory, with which the writer has been concerned, in which special attention has been directed to the above aspects of fatigue. Unless otherwise stated, the metal under test was in the usual form of a finely-divided crystalline aggregate. The tests were all made under ordinary atmospheric conditions. The terms "safe" and "unsafe" are used to define those ranges of stress which would not or would produce fracture if applied for an indefinitely great number of repetitions.

### 1. Cyclical Stress-Strain Relations.

The general nature of the stress-strain relations obtaining during cyclical variations of stress is now fairly well established. The work of Bairstow,<sup>3</sup>

<sup>1</sup> Haigh, *J. Inst. Metals*, **2**, 1917.

<sup>2</sup> McAdam, *Proc. Amer. Soc. Test. Mat.*, **26**, 2, 1926.

<sup>3</sup> Bairstow, *Phil. Trans.*, **A. 210**, 1910.

on iron and steel, of Hankins<sup>4</sup> on nickel, of Gough and Hanson<sup>5</sup> on Armco iron, and Gough<sup>6</sup> on copper, covered the three general cases : (a) range of primitive elastic limits of material greater than the safe range of reversed stresses, (b) safe range of reversed stresses exceeding the range of the primitive yield points, and (c) the metal possessing no primitive elasticity, although exhibiting a clearly-defined safe range of stress. As a result the cyclic stress-strain relationships during a fatigue test can be summarised briefly as follows: During the first few cycles, relatively large unclosed loops are observed whose widths tend to diminish with subsequent cycles; alternatively, a loop of very small width is observed whose width does not vary greatly during the first few cycles. These stages are marked by the development of permanent strain. If the applied range of stress is less than the limiting range, at some stage, further permanent strain will not occur. Strain hysteresis will, however, be present, and will persist, as far as is known, indefinitely (I have found this state of elastic hysteresis to persist, unchanged, in Armco iron for 100,000,000 cycles of stress). Should the safe range be exceeded, then the loop will never entirely close, although it may appear to do so. Elastic hysteresis and plastic strain are both operating. At some later stage, the rate of increase of permanent set and of cyclical permanent set both usually increase and fracture ultimately results. This last stage may be confined to a few cycles only or to a very much greater number, and is almost certainly connected with the propagation of small fatigue cracks throughout the mass of the specimen. Now these typical phenomena can be accounted for entirely by either one, or a combination, of plastic deformation and elastic hysteresis. That a state of elastic hysteresis can persist indefinitely without causing cumulative destructive effects on the metal must now, in view of the observations of many independent observers, be definitely accepted. It is, obviously, a process by which, the metal is capable of transforming an indefinitely large amount of strain energy into thermal energy, and this has been demonstrated, experimentally, by many observers, by means of calorimeters, thermo-couples, etc. It has been said that strain hysteresis is an effect peculiar to crystalline aggregates, having its origin at crystal boundaries. To examine this possibility, the writer and his colleagues made a very carefully conducted experiment<sup>7</sup> on a large single crystal of aluminium (diameter  $\frac{1}{4}$  inch, length 7 ins.). The specimen was subjected to cycles of repeated tensile loading; an extensometer of very great precision being employed. It was found that the cyclic stress-strain relations observed were precisely similar, in all respects, to those previously found when crystalline aggregates were tested. Following the usual preliminary plastic strains, the specimen gradually attained a cyclic state involving large strain hysteresis without further permanent set. The hysteresis loop was of the usual well-known shape obtained with crystalline aggregates. Hence, it must now be accepted that strain hysteresis is a property exhibited by crystalline matter which has been subjected to previous plastic deformation and cannot be ascribed simply and solely to boundary effects in aggregates. The test also showed that the crystal possessed no appreciable initial range of elasticity; a single application of a tensile stress of 0·1 tons/inch<sup>2</sup> produced measurable permanent strain.

<sup>4</sup> Hankins, No. 789, *Repts. and Memoranda Series, Aeronautical Research Committee*, Nov. 1921 (H.M. Stationery Office).

<sup>5</sup> Gough and Hanson, *Proc. Roy. Soc., A.* 104, 1923.

<sup>6</sup> Gough, *Engineering*, 8th Sept., 1922.

<sup>7</sup> Gough, Hanson, and Wright (a) *Phil. Trans., A.* 226; also (b) No. 995, *Repts. and Mem. Series, Aero. Res. Ctee.*, Nov. 1924.

## 2. Fatigue Tests on Crystalline Aggregates; Deformation by Slip.

Twenty-eight years ago, Ewing and Rosenhain<sup>8</sup> showed that if a metal is deformed by straining, its structure remains essentially crystalline, plastic yielding being due to slipping along cleavage or gliding planes within the crystals. The effect of alternating stresses on the microstructure of metals was first studied by Ewing and Humfrey<sup>9</sup> in 1903. They observed the growth of slip bands produced by ranges of stress which eventually produced failure. These slip bands increased in number and broadened out with reversals of stress. Failure was attributed to a process of attrition along slip planes resulting in a collection of débris which was squeezed out from the crystals. The crack thus formed spread from crystal to crystal leading to ultimate rupture of the specimen. Stanton and Bairstow<sup>10</sup> also made a study of the failure of metals under alternating stresses; their microscopical observations were confined to specimens subjected to stress ranges of such an intensity as to cause failure. It was no doubt due to the fact that, in all these experiments, the stress ranges employed exceeded the limiting range which in turn was less than the range of the primitive elastic limits of the materials employed that the results obtained were considered to be compatible with the "attrition" theory of fatigue. Now the attrition theory assumes that the material in a plane on which slipping has occurred is thereby rendered less resistant to further slipping than the material in the neighbourhood of the slip plane which has not yet deformed plastically. The subject was re-opened in 1921 by a research<sup>1</sup> carried out by the writer and a colleague. A study was made of the effects on the microstructure of metals deformed by statical stresses and by safe and unsafe ranges of alternating stresses. The metals employed included Armco iron, copper, and mild steel subjected to reversed and alternating direct stresses, also reversed bending and reversed torsional stresses. Some of the experimental facts determined were as follows: (a) Strain hysteresis was found to be present under repetitions of all the stress ranges investigated irrespective of the fact that the range was safe or unsafe. (b) Permanent set was detected on the removal of statical tensile stresses of less intensity than the limit of proportionality as ordinarily determined. (c) Slip bands were produced by stress ranges which were considerably lower than the limiting range of stress; this applied to all the metals investigated under every type of applied stress. (d) No marked differences could be detected in the effects on the microstructure of safe or unsafe stress ranges prior to the cracking stage. (e) Broad dark bands, presumably similar to those observed by Ewing and Humfrey,<sup>9</sup> were produced by safe stress ranges: in many cases, however, it was found possible to resolve these bands into a mass of very fine slip bands. (f) The most careful examination failed to discover the critical stage at which fatigue cracks first formed: once formed, however, observations of the progress of these cracks indicated that their propagation was due to stress concentration effects, a process probably totally different from that of the earlier stages of fatigue failure.

It appeared to us that these experimental observations led to the inevitable conclusion that plastic deformation caused by alternating stresses must be a strengthening or hardening influence (hardening is used in the sense that resistance to further plastic deformation by slip is *increased*). That such hardening is caused by severe statical stressing was, of course,

<sup>8</sup> Ewing and Rosenhain, *Proc. Roy. Soc.*, 1899.

<sup>9</sup> Ewing and Humfrey, *Phil. Trans.*, A. 200, 1903.

<sup>10</sup> Stanton and Bairstow, *Proc. Inst. Civ. Engrs.*, 166, (1906).

well known; it now appeared certain that the same effect could now be produced by fatigue stressing. Moreover, such hardening occurred when the applied range of stress was less than, equal to, or greater than the safe range of stress. The initiation of the fatigue cracks was ascribed to the capacity of the material for cold working having been exceeded locally at various places throughout the mass; this is known to occur in wire-drawing operations. Shortly afterwards, Aitchison<sup>11</sup> made some tests to find out if fatigue stressing produced the hardening effects suggested by us. He used specimens of steel, brass, and copper which had been subjected to cycles of direct stresses—some to fracture, others for several millions of cycles. Ball hardness determinations were made on the unstressed as well as on the stressed portions of these specimens. In each case he found a considerable increase of hardness had resulted from the fatigue stressing and commented ". . . from the results it follows that the application of fatigue stresses to the metals results in hardening by an amount that may be just as great as that resulting from the application of very considerable static stresses, and that this hardening is accomplished without any plastic distortion in the ordinary sense.\* Presumably it is the effect of the internal slipping observed to occur by Gough and Hanson."

Now any experiments performed on finely-divided crystalline aggregates involve uncertainty in some respects. Stress calculations as usually computed are only approximate values when any individual crystal is concerned, as the condition of continuity of structure demanded by the laws on which these calculations are based are not fulfilled. Further, the unknown nature of the intercrystalline boundary is an additional complication. Fatigue tests on single crystals thus indicated a promising field of research and, in 1923, owing to the kind co-operation of Professor Carpenter and Miss Elam, we were able to commence work on large single crystals of aluminium.

### 3. Fatigue and Other Tests on Single Crystals of Aluminium.

The objects of the first research<sup>7</sup> were an investigation of the changes in microstructure and of the nature of the deformation of single crystals subjected to (a) alternating direct stresses, (b) alternating torsional stresses, (c) slow cyclic repetitions of tensile stress, and (d) single-blow impact-tensile tests. Changes in microstructure and the form of the specimens were studied in their relation to the crystalline structure and to the applied stress system. The broad results of the investigation can be summarised under several headings as follows:—

(i) *Mechanism of Deformation.*—Under all the stressing systems employed, the mechanism of deformation of aluminium crystals was one of shear along certain crystallographic planes in certain crystallographic directions lying in these planes. The slip planes were the planes of maximum atomic density (octahedral planes) for this space-lattice (face-centred cubic), while the direction of slip, in every case, coincided with that of one line of greatest linear atomic density (principal lines of atoms). As there are four sets of octahedral planes, each of which contains three principal lines of atoms, there are always available twelve possible lines of slip, or twenty-four directions. The plane and direction of slip were always determined by the condition that the shear stress on the plane resolved in the slip direction was a maximum for all possible slip directions. This is precisely the same condition as that found, previously, by Taylor and Elam,<sup>12</sup>

<sup>11</sup> Aitchison, No. 923, *Repts. and Mem. Series, Aero. Res. Ctee.*, May 1924.

\* Dr. Aitchison means distortion of the specimen as a whole.

<sup>12</sup> Taylor and Elam, *Proc. Roy. Soc., A.* 102, 1923.

to govern distortion under static tensile loading and, also, compressive loading, as shown later, by Taylor and Farren.<sup>18</sup> Thus it is now known that the distortion of single crystals of aluminium, whether caused by statical, fatigue or impact forces, is controlled by one simple stress condition and this appears to be a decided advance towards the simplification of the strengths of materials.

(ii) *Strain Hysteresis*.—It has been mentioned above that the cyclic stress-strain relations of a single crystal proved to be identical with those previously met with in crystalline aggregates; further, the crystal possessed no appreciable range of primitive elasticity under tensile loading, measurable plastic deformation occurring on the application of very small stresses ( $0.1$  tons/inch $^2$ ).

(iii) *Observations on Slip Bands formed during Fatigue Tests*.—All the ranges of stress employed produced slip bands which were identified as the traces of slip planes on the surface of the specimen. If the applied stress range was less than the limiting range and the surface of the specimen was repolished after a small number of repetitions of stress, little further slip appeared. After a further repolishing, subsequent cycles produced no slip bands, the material now, apparently, being completely strengthened or hardened against further deformation by shear under the applied stress range. If the applied range was increased in magnitude, further slip became visible and the *spacing* of the slip bands was closer than that of the previous bands. Subsequent repolishing and straining produced the same effects as with the lower range of stress, the same hardening effects being disclosed. When the range of stress was such that it led to ultimate fracture, the slip band phenomena were not very different in their general characteristics. A much closer-spaced system of slip bands appeared, but frequent repolishings of the specimen during the test showed that the progressive hardening process still continued even though fatigue failure was in action. In one test on a specimen subjected to reversed direct stresses, it was found that the character of the surface markings appearing in the later stages of the test differed very appreciably from those previously observed. These markings were of an irregular, wavy, nature not easily identifiable with the crystalline structure of the material. The slip band phenomena exhibited by these single crystals were, therefore, similar in many respects to those observed in our previous work on crystalline aggregates. The single crystal is also capable of being "cold-worked" by fatigue stressing and is thereby enabled to resist further deformation by shear under the same range of load. This process appears to go on under both safe and unsafe ranges of stress. But, in the latter case, some other action intervenes at some stage and causes fracture in some way which is not apparently directly related to the previous plastic deformation by slip. It appears extremely probable, however, and based on certain experimental facts, that the mechanism of fracture occurs as an *indirect consequence* of the previous deformation. There are some features which are of especial importance in their relations to cohesion problems in general. The fact that the crystal has no appreciable range of primitive elasticity is a most unexpected result. Also, it appears certain that our "single" crystals do not even approach a state of homogeneity even when a system of parallel crystallographic planes is considered. The structure appears to be divided into portions of varying resistance to deformation by shear, yet the locations of these portions possessing different strengths do not appear to be hap-

<sup>18</sup> Taylor and Farren, *Proc. Roy. Soc., A.* III, 1926.

hazard. For, although the average spacing of the slip bands (as judged by the number visible in any given field) caused by a range of stress appears to be controlled by the value of the applied stress range, yet any one set of slip bands (particularly those formed under a safe range of stress) appears to conform to a very fair degree of uniform spacing. It is difficult to account for this behaviour by ascribing it to the *distribution* only of the impurity atoms known to be present. For, if these were distributed *uniformly* throughout the crystal, why should the pitch of the visible slip bands be apparently some function of the value of the applied shear stress? On the other hand, if the distribution of the impurity atoms is *not* uniform, how is the regularity of the slip bands, seen at any one stage of the test, to be accounted for? In discussing this matter recently with a colleague (Mr. Cox), it occurred to us that the behaviour might be accounted for if each of the various types of impurity present is distributed regularly through the crystal, the atoms of each type acting as a nucleus of extremely local crystallisation, probably different (crystallographically) from that of the parent crystal. We see many possible objections to this idea, but it seems to be worth advancing for criticism. As a general argument against attaching too much importance to the theoretical consequences of impurities in the present connection may be mentioned the general experience encountered with metals, *viz.*, that the higher the degree of purity, the greater is the state of ductility obtained.

(iv) *Hardening caused by Slip.*—When a single crystal of aluminium is subjected to a static tensile strain or to a range of alternating direct stresses, the plane and direction of slip are controlled by the maximum resolved shear stress condition referred to above. In the general case the specimen increases in length and the axis of the specimen moves relatively to the crystallographic axes in a path directed towards the direction of slip. This results in an *increase* in the value of the maximum resolved shear stress (the average distortion being one of simple shear, the area and shape of the *slip plane* remains constant during the deformation, although the shape and area of the cross-section of the *specimen* change). Thus as a result of the slipping the force producing slip has increased; yet we find that the amount of slip, produced by a safe range of alternating stress, is definitely limited. It is apparent, therefore, that not only does slip on a plane produce increased resistance to further slip on the same plane, but the action is self-stopping and the hardening must proceed at a greater rate than the slipping which produces the hardening. Now in aluminium there are present three sets of possible slip planes in addition to that on which slip is proceeding. A diagram<sup>7</sup> can be drawn showing how the shear stress on all these planes varies during the deformation, and it can be shown that the stress on, at least, one of these alternative planes increases at a quicker rate than on the slip plane. Yet, except for very slight disturbances in the very early stages of the deformation no slip occurs on these alternative planes until the stress on one of these planes becomes actually greater than that on the original slip plane. This shows clearly that the hardening due to slip is not confined to the actual plane of slip, but that the crystal is hardened in other directions. Again, at some stage (in the general case) of the deformation, the specimen axis becomes equally inclined to sets of octahedral planes, on one of which the previous slip has occurred. Further deformation then proceeds by a process of alternate slip on these two sets of planes, and the nature of the resulting deformation is such that these planes possess approximately equal resistance to deformation by shear. Now we know that the original plane of slip has been

very greatly hardened by the previous deformation and, hence, it is apparent that the second set was hardened during the same stage even though they did not act as slip planes. It appears to me that these experimental facts throw considerable doubt on the hypothesis that layers of hard amorphous material formed on slip planes are responsible for increased hardness; it seems reasonable to suppose that the resistance to shear in directions parallel to and transverse to such hard layers would differ greatly.

The failure of single crystals of aluminium under reversed torsional stresses is of particular interest. While conforming to the maximum resolved shear stress law governing the deformation, the type of distortion is such that the cross-section of the specimen divides itself into zones in each of which slip is confined to one set of octahedral planes and along one particular principal line of atoms. It is possible to fracture a crystal under these conditions without producing any change in the relative orientations of the specimen and crystallographic axes. (The slip phenomena observed are precisely similar to those produced by other fatigue straining actions.) If a specimen, to which reversed torsional stresses have been applied (thus producing fracture), is cut across transversely to the axis, the hardness of various parts of one of the zones, described above, may be explored by means of indentation tests.<sup>14</sup> In such a zone, the applied stresses have varied from zero to a value exceeding the safe range. It was found that the degree of hardening obtained at any point was roughly proportional to the range of stress previously applied at that point, irrespective of whether that range was a safe range of stress. Therefore, with our "single" crystals, as with the crystalline aggregates, it is apparent that the safe range of stress does not mark that point at which the hardening of the metal, as a whole, by plastic deformation reaches a maximum. But all our experience has shown that fatigue cracks first become visible in those regions which have suffered maximum plastic distortion as judged by the intensity of the slip band markings. It therefore appears to be most probable that fatigue cracks occur as an indirect consequence of distortion. Now if hardening results in severe lattice distortion in local regions, an applied system of alternating stresses might produce principal stresses<sup>15</sup> of such an intense nature as, conceivably, to initiate small sub-microscopic cracks and cause their propagation without further plastic deformation. If this could happen, it should be possible, theoretically, to harden up a crystal specimen—by cycles of stress slightly exceeding the safe range—to such an extent that the last stages of fracture would consist merely of a joining-up of sub-microscopical cracks, or the spreading of cracks due to stress concentration effects: in either case principal stress would be the agent and slip bands would not, necessarily, be produced. To explore this possibility experimentally, a crystal specimen<sup>14</sup> was subjected to cycles of a range of reversed torsional stresses whose value (nominal stress =  $\pm 1$  ton/inch<sup>2</sup>) was estimated to produce a lengthy endurance before causing fracture. Stress analysis showed that three sets of octahedral planes would be involved in the deformation. The specimen fractured after 9,275,000 reversals of stress. The surface of the specimen was examined, photographed, and repolished after 0, 54,000, 110,000, 204,000, 1,082,000, 2,854,000, and 7,204,000 stress reversals had been applied. Examination at these various stages showed that the process of progressive hardening was in action throughout, as revealed clearly by the decrease in the areas of visible slip. At different

<sup>14</sup> Gough, Wright, and Hanson, *J. Inst. Metals*, **36**, 2, 1926.

<sup>15</sup> Southwell and Gough, *Phil. Mag.*, I, Jan. 1926.

stages slip ceased on one set of octahedral planes and, later, on the second set. Examination after 7,204,000 reversals revealed a few traces only of slip on the most highly stressed set of planes. These were removed by polishing and the specimen fractured after a further 2,071,000 reversals, and the most careful examination of the surface failed to reveal any slip bands in the neighbourhood of the fracture. Evidently *the propagation of the fracture had occurred without visible slip.*

#### **4. Effect of Hardening by Slip on the Crystalline Structure, and a Working Hypothesis of Fatigue Phenomena.**

In endeavouring to estimate the effects caused by slip on crystal structure we at once enter very debatable ground. Practically the only evidence that can be obtained depends on the interpretation of certain X-ray phenomena. Whereas an unstrained crystal gives sharply-defined X-ray reflections, permanent strain produces reflections that are broadened in one direction. Now, the X-ray analyses of our specimens (made from photographs taken while the specimen is rotated through a complete revolution about its axis) show that the original continuous crystalline structure is not *substantially* changed. Moreover, if the specimen is subjected to further plastic deformation, the resulting distortion is also consistent with this condition. Thus it does not appear probable that deformation caused by alternating stresses can result in a uniform curvature of the slip planes. To reconcile the nature of the X-ray reflections with the hardening produced by fatigue stressing, we suggested<sup>10</sup> that the slip plane, after slip, is in a "buckled" or "rumpled" state, containing crests and hollows, the direction of buckling being confined to the slip direction and the mean curvature of the plane remaining at zero value. Subsequently, in a comparison<sup>10</sup> of the results of the work of Carpenter, Taylor and Elam, Muller, Goucher, with our own results, it appeared to me that a measure of agreement had been reached that crystal break-up is the cause of hardening produced by plastic strain. After such break-up the structure may consist of a number of smaller crystals, probably more perfect than the parent crystal, and possessing crystalline orientations differing but slightly from that of the parent crystal. In this process of break-up, the crystallites have probably rotated slightly in either direction about an axis perpendicular to the direction of slip. With increasing deformation the process is extended. There appears to be available as yet no evidence of the mechanism by which this rotation is accomplished and, until this rotation is established, it is perhaps dangerous to speculate on its effects. Nevertheless a fairly satisfactory working hypothesis of fatigue can be built up based on hardening caused by crystal break-up and the slip-band phenomena observed in the researches summarised above.

Consider a perfect single crystal of absolute structural regularity and perfect purity. Such a crystal would be expected to withstand, elastically, a range of shear strain very greatly in excess of any yet applied, experimentally, to a "single" crystal or a crystalline aggregate. Now we have found, experimentally, that our "single" crystals of aluminium possess an extremely small range of initial elasticity. The slip band phenomena encountered suggest that the crystal is not uniformly weak but consists of portions or layers possessing varying degrees of resistance to shear strain, while layers of equal resistance are distributed in a fairly regular manner

<sup>10</sup> Gough, *Metallurgist (Supplement to Engineer)*, Sept. 24, 1926.

throughout the mass. If these conditions actually obtain and if plastic deformation causes crystal break-up, then one would expect increasing severity of applied straining to produce increasing refinement of sub-structure, each crystallite, at any stage, enclosing material of greater stability under shear strain than that which was situated, prior to the application of the strain, at the present boundaries of the crystallites. The severing of atomic bands involved in this process would account for the heat bursts noticed by Stromeier,<sup>17</sup> and Hankins,<sup>4</sup> and for the fact—first observed by the latter investigator—that such heat bursts do not reappear under subsequent repetitions of the same range of strain. Further, the progressive hardening that would be produced is consistent with the slip band phenomena and ball indentation tests previously described. As the applied range of strain increases, the sub-structure should become of increasing refinement, the crystallites approaching more nearly towards the strength of ideal single crystals, as at present understood, each stage of approach being accompanied by increased resistance to plastic deformation by shear. This process appears to be capable of extension to a much greater degree than that accompanying the relatively small range of strain required to produce fatigue failure in existing metals and, as far as hardening effects are concerned, the researches of the writer and his colleagues have shown that hardening is indeed carried beyond this stage. Initiation of fatigue cracks and strain hysteresis effects are not likely, therefore, to originate within the crystallites themselves. But X-ray data have been interpreted as indicating that slight differences of orientation exist between neighbouring crystallites. It appears, probable, therefore, that in the regions separating these crystallites, there are many atoms which have alternative positions of stability. Under a certain range of shear strain of the material as a whole, these particular atoms would, after a certain degree of elastic strain, move over to their alternative stable positions, and the combined action of many such movements appears consistent with the strain hysteresis effects which have been found to occur. Cyclical movement of this type would thus account for the state of elastic hysteresis, in which state the material can apparently transform strain energy from the external straining system into thermal energy without involving cumulative damage to the material. But it would be expected that following greater plastic deformation, the relative orientation of neighbouring crystallites would exceed a critical value of lattice distortion consistent with cyclic movement of this type. Local discontinuities of structure would then exist which, under strain ranges of sufficient magnitude, might initiate sub-microscopic cracks leading to the progressive fracture of the metal. In spite of the speculative nature of this conception of the initiation of the fatigue crack, certain experimental facts appear to be consistent with the suggested process. For example, fatigue cracks in an aggregate while undoubtedly having their origin in regions of marked previous plastic strain afterwards follow path, which are not confined to such regions. Again, when single crystals fail under fatigue, the cracks commence in the regions of greatest resolved shear stress, but afterwards follow paths that may have no apparent relation to the slip planes. We have seen, also, that it is possible to harden a crystal under an unsafe range of stress to such an extent that the final stages of fracture are not marked by the development of visible slip.

<sup>17</sup> Stromeier, *Proc. Roy. Soc., 90*, 1914.

### 5. A Speculation Regarding the Nature of Inter-crystalline Boundaries in Crystalline Aggregates.

From the foregoing considerations of crystal break-up, it appears probable that the limiting strain which can be applied to metals—in the form as available—is very small if lattice distortion *only* is to be the result. This offers an interesting possibility regarding the nature of an inter-crystalline "boundary." It has been suggested that the change of orientation between neighbouring crystals in an aggregate is achieved by lattice distortion only, resulting in a gradual transition of orientation. It appears improbable that, in the limited area available for this transition, such marked changes of orientation, as have been known to exist, could be effected without the limiting lattice distortion being exceeded. Much greater, however, is the probability that the inter-crystalline zone is occupied by a large number of very small crystallites, the orientation of adjacent crystallites being slightly different, and the system being so arranged that the required change of direction from crystal to crystal is achieved by an integration of small changes. As far as I am aware, this suggestion has not previously been advanced and is now offered for criticism.

Now, a boundary of the nature suggested should be very stable under applied stress at temperatures far removed from the melting-point of the metal, and this is consistent with common experience of the strength of most metallic aggregates at air temperatures. But in view of the lattice distortion that would exist between adjacent crystallites the effect of increased temperature would be expected to produce distinctive characteristic effects which would be most marked at the inter-crystalline boundaries. For instance, recrystallisation effects would be expected to originate at such boundaries, and some of Professor Carpenter's work on grain growth is very significant in this respect. Again, as the temperature of test is raised, movement at boundaries under external stressing systems should become much more marked than at air temperatures; recent researches have disclosed the experimental facts, whatever may happen to prove eventually the cause of these phenomena. Again, the recent researches of McAdam, on *corrosion-fatigue*, showed that the path of fracture, "in its path from one inclusion to another, sometimes deviates and, for a short distance, follows intercrystalline boundaries."<sup>2</sup> The marked effects of *static* load applied in the presence of a corrosive agent on the boundaries is, of course, well known.

### 6. Some Effects of the Intercrystalline Boundaries in Metallic Aggregates.

The experiments which have been described show that very similar phenomena are exhibited by crystalline aggregates and single crystals under fatigue action; the effect of the crystal boundary remains obscure. A series of experiments is in hand by which, by employing aggregates of various grain sizes, it is hoped to obtain some information on this point. The results of two experiments of this nature may be of interest.

A specimen of aluminium containing three large crystal grains was submitted to various ranges of reversed torsional stresses. The surface was examined at various stages and the usual progressive hardening processes were observed. In those portions of the crystals not near crystal boundaries, the slip bands observed were similar in all respects to those observed in similar tests on single crystal specimens. Where the slip bands

on either side of, and near to, a crystal boundary did not differ greatly in inclination, neither crystal exercised any marked shielding effect on the other, and the slip bands extended, in most cases, right up to the boundary. Where this occurred it was difficult to etch up the boundary; the neighbouring crystals were probably of very similar orientation. Where the slip bands on either side of a boundary had very different orientations a distinct shielding effect was noticed. The greater portion of the slip bands stopped short of the boundary while those which approached it more closely changed their directions in so doing. The main fracture was confined to one crystal; where it eventually spread into neighbouring crystals the crack intersected the boundary nearly at right angles.

Thus the test showed, broadly, that the effect of the boundary was mainly one of "interference" due to the differing orientation of neighbouring crystals. The fatigue strength of the specimen seemed to be controlled partly by the strength of the weakest crystal present and partly by the shielding effect of the boundary.

Some experiments have also been made upon the effect of fatigue stressing upon the density of aluminium. A series of specimens were tested under alternating direct stresses, some to fracture, others under safe ranges. One batch of specimens was in the form of single crystals. A second batch was made from material which had been submitted to precisely the same thermal treatment as that employed in the preparation of the single crystals, but had not received the intermediate critical strain. They were thus in the form of a finely-divided aggregate. The density of each specimen was determined both before and after applying the fatigue test, the most refined methods being employed; the density determinations can be relied upon to one part in three thousand. The results showed definitely that no change occurred in the single crystal specimens due to the application of safe or unsafe ranges of stress. On the other hand a decrease of density which varied from 0·037 per cent. to 0·100 per cent. of the density in the unstressed state occurred with the polycrystalline specimens. It appears, therefore, that a decrease in density of a metallic specimen due to cold-working by fatigue marks an effect which is confined to the neighbourhood of the crystal boundaries or is caused by the presence of such boundaries. Where no such boundaries exist, as with the mono-crystalline specimens, changes of density do not occur.

Space will not permit of reference to other researches relating to such aspects of fatigue as the effects of the presence of discontinuities causing stress concentrations, of ductility on fatigue strength, of the effect of flaws on the propagation of fatigue fractures, etc., and those interested are referred to the original publications.<sup>18, 19, 20</sup>

<sup>18</sup> Gough Wright, and Hanson, No. 1025, *Reports and Mem. Series, Aero. Res. Ctee.*, Jan. 1926.

<sup>19</sup> Gough and Tapsell, No. 1012, *Repts. and Mem. Series, Aero. Res. Ctee.*, April 1926.

<sup>20</sup> Gough, H. J., No. 864, *Repts. and Mem. Series, Aero. Res. Ctee.*, April 1925.

## COHESION IN SURFACE FILMS.

By N. K. ADAM.

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*Structure of the Films.*—A summary of the evidence as to the structure of monomolecular surface films, of long chain substances, on water was given at the Discussion on Physical Phenomena at Interfaces last year.<sup>1</sup> There are three principal states of the films, the condensed (close-packed, nearly vertically oriented molecules); the gaseous, in which the molecules are flat in the surface and moving about more or less independently; and the expanded, which are intermediate in area and properties between the condensed and the gaseous types. The orientation of the molecules in the two types of "expanded" film described last year is still undecided. Two points of structure demand attention here, on account of fresh considerations which have arisen since last year.

*Liquid Expanded Films.*—As a result of work done during the past year, now nearly completed, I think the structure proposed last year must be abandoned. This was that the molecules had the chains coiled in helices with vertical axis, in contact and cohering. The main reason for proposing this structure was that in the first dozen or so liquid expanded films of which the area at no compression had been accurately measured, the area was always very close to 48 sq. Å.U. There appeared to be some peculiar structure of the chains which occurred in all these films, determining a constant area, and the only possible structure seemed to be that of coiled chains. Two liquid expanded films have now been found, one with a decidedly smaller area, and another with a much greater area, depending on the nature of the head of the molecule, and the necessity for this hypothesis vanishes.

I am inclined to adopt Professor Garner's suggestion<sup>2</sup> that the chains have a considerable tilt in these films, though it remains to be discovered why there should be a definite state of the films at one tilt, and that a considerable one, between the vertical, condensed state, and the horizontal, gaseous state. The cause of the existence of this state remains a rather difficult problem, and means of experimental attack on it seem rather restricted.

*Films with Close-packed Heads may have Tilted Chains.*—Müller<sup>3</sup> suggests that in those films in which I have supposed the chains to be slightly separated by the heads being closely packed, the chains are tilted. I think that the area of this class of condensed film is so definitely determined, in nearly all cases, by the nature of the heads, that one must suppose the packing of the heads to be primarily responsible for the area of the film. It seems however very likely that the chains, finding themselves kept slightly apart by a rather wide spacing of the heads, will tilt so as to pack the available space as closely as possible. I would therefore agree with Müller's hypothesis of tilted molecules, but say that probably the peculiar properties of each

<sup>1</sup> *Trans. Far. Soc.*, **22**, 472 (1926).

<sup>2</sup> *Ibid.*, **22**, 498 (1926).

<sup>3</sup> *Proc. Roy. Soc. A*, **114**, 559 (1927).

head determine primarily the spacing of the heads, and secondarily the tilting of the chains; also that it seems likely that the areas at no compression are actual measures of the cross-section of the heads, as packed in the films.

Müller says that there seems no theoretical reason for the high compressibility of the film, in the region which I have called the transition between close-packed heads and close-packed chains. My original suggestion seems however to suffice, that the molecules slide over one another slightly, perpendicular to the surface, until the heads find recesses in the chains into which they can be forced by compression until they no longer keep the chains apart. It would be difficult, in films only one molecule thick, to exclude such slipping of the molecules, and the zigzag nature of a carbon chain must provide numerous such recesses. The high compressibility of the films with close-packed heads does not, however, invariably occur; the benzene derivatives do not show it nor cholesterol, these films being very incompressible; in these cases the heads are long, in the direction of the chains, as well as wide, and probably the recesses in the chains are too small to allow any tucking away of the heads.

*Rigidity may be due to Cohesion between End Groups Alone.*—In one case at least, the urea derivatives, the films with close-packed heads are solid films; that is, they have rigidity in the plane of the surface. The area is 25·5 sq. Å.U, and the film is very incompressible. If the thickness is taken as three atoms, the compressibility is of the same order as for organic substances in bulk. The film is probably therefore not re-arranged by compression, but is maintained solid and with the heads apart mainly, or, entirely, by the cohesion between the NH . CO . NH<sub>2</sub> groups at the end of the molecule. This solid structure must be one of the thinnest solids known. It breaks down at a certain transition temperature, allowing the chains to come into contact. This temperature may be regarded either as the transition temperature between two "allotropic" condensed films, or as the "melting-point" of the two-dimensional structure three atoms thick, showing that allotropy may be strictly analogous to melting, a part only of the crystal lattice structure giving way under the thermal agitation.

*Rigidity Partly Determined by Length of Chains in Contact.*—With chains of about 18 carbons in length, the solidity or otherwise of the films depends mainly on the end group. Thus the phenol is solid, and the urea (below the transition temperature); the acid is also solid (though supercooling sometimes seems to take place so that the film deposited from solution is not quite always solid); but the octadecyl alcohol is apparently always a liquid film. With chains of about 30 carbons, however, the films are rigid even with the alcohols.

*Closeness of Packing Determined by Length of Chains, Superposed on an Effect due to Lateral Attraction between Heads.*—A perfectly gaseous film, with substances of long enough chains to be insoluble in water, is unknown. The ester H<sub>5</sub>C<sub>2</sub>OOC . (CH<sub>2</sub>)<sub>11</sub> . COOC<sub>2</sub>H<sub>5</sub> approaches most nearly to the perfect gaseous condition of any yet examined. With this substance, and still more with others, there are departures from the perfect gas "surface pressure-area" curve (corresponding to the isothermal of a gas), of the same nature as the cohesionless corrections to actual gases. In the homologous series of the simple fatty acids, the amount of this cohesionless correction increases regularly with increase in the length of the chain. Thanks to the studies of Schofield and Rideal,<sup>4</sup> we are able to trace the effect of this cohesionless correction far down into the region of soluble, ad-

<sup>4</sup> Proc. Roy. Soc., A. 109, 57 (1925); 110, 167 (1926).

sorbed films, and the effect of increasing the length of the chain is the same in the soluble as in the insoluble region.

In the condensed films, the effect of length of chain on the cohesion is very evident. Addition of a given number of carbons to the chain raises the temperature of expansion, at which the condensed film breaks down, forming an expanded, or occasionally a gaseous film, by a definite amount independent of the nature of the head of the molecule. This is about  $10^{\circ}$  near  $0^{\circ}$ , and  $7^{\circ}$  near  $60^{\circ}$ , for each additional carbon. Evidently a greater degree of thermal agitation is necessary to break up the close packed, parallel chain structure, the longer the chains which are in contact.

It is obvious, however, from the following table, that the nature of the heads determines the expansion temperatures for each homologous series, and therefore makes a considerable contribution to the lateral adhesion between film molecules. The substances in the first part of the table all have 16 carbon atoms in the hydrocarbon chain; nevertheless, excluding the phenol, which has the benzene ring in continuation of the chain, and the urea, which has the 3 atom chain  $\text{NH CO NH}_2$  at the end, the temperature of expansion ranges from about  $0^{\circ}$  to  $46^{\circ}$ . We may therefore place the end groups in the following order of decreasing lateral adhesion:  $\text{CH}_2\text{OH}$ ,  $\text{CONH}_2$ ,  $\text{CH : NOH}$ ,  $\text{COOH}$  (unionised),  $\text{COOCH}_3$ ,  $\text{COOC}_2\text{H}_5$ ,  $\text{CN}$ ,  $\text{CHBrCOOH}$  (unionised), ionised  $\text{COONa}$ . No doubt the lessened attraction between acid molecules when on soda is due to the development of similar electrical charges on adjacent molecules.

*Temperatures of Half Expansion Under 1·4 Dynes Per Cm.*

Substance.	Temperature. Degrees.
Palmitic acid on N/10 soda . . . . -	6 (roughly)
$\alpha$ -bromopalmitic acid on HCl . . . .	3
Palmitic nitrile . . . .	6·5
Ethyl palmitate . . . .	13
Methyl palmitate . . . .	27·5
Palmitic acid on HCl . . . .	28·5
Palmitic aldoxime . . . .	33·5
Palmitic amide . . . .	36
Hexadecyl alcohol . . . .	46
Hexadecyl urea . . . .	48·5
$\beta$ Hexadecyl phenol . . . .	55

*Unsaturated Chains with Double Bond in Middle of Chain.*

Oleic acid on HCl . . . . .	- 30 (extrapolated from results on erucic acid, but probably nearly correct)
Elaidic acid on HCl . . . . .	- 0·5
Iso-oleic acid ( $\text{F}_{\alpha\beta}$ ) on HCl . . . . .	25

*Balance Between the Attraction of the Chains to Each Other and to Water.*—The last three substances show the effect of double bonds in various positions in the chain. The compounds have 18 carbons in the chain, and the temperatures of the corresponding compounds with 16 carbons, which should be compared with the earlier ones in the table, would be some  $20^{\circ}$  lower. Evidently the double bond has an enormous effect in lowering the expansion temperature, especially if it is of the oleic type, and in the middle of the chain. The elaidic stereoisomeric type has less effect. It is difficult to ascribe much of this lowering of the expansion temperature to a diminished attraction between the parallel chains in contact, for in the oleic type the temperature is lowered some  $55^{\circ}$  merely by

the presence of the double bond half-way up the chain. It seems more probable that the double bond actually increases the attraction for water to such an extent that the condensed film becomes much less stable than with saturated chains. If the attraction for the double bond is still further increased by adding permanganate to the water, the film becomes gaseous, if the double bond is in the middle of the chain; there is no case of a film with the double bond in this position being condensed, or even expanded, on permanganate. This is fairly easy to understand, as the molecules lie flat in the gaseous films. The films of oleic acid on HCl are however liquid expanded, with a very low vapour pressure, and exactly how the attraction between the double bond and the water can operate to promote the "expanded" state is not clear. In his first paper, Langmuir noted this effect of the double bond; but I do not think the suggestion made there, that the double bond simply provided a second "point of attachment" additional to the COOH group can explain the facts, for if it were so the still stronger second point of attachment caused by permanganate in the water would also produce an "expanded," not a gaseous film. In my experience, a second definite point of attachment remote from the first makes the molecules lie flat and the film is gaseous, not expanded.

*Balance Between Cohesive Forces and Thermal Agitation.*—In the surface films, as always in matter, the stability is a result of a balance between forces acting in opposite directions. The cohesive forces tend to maintain that structure in which the attractions are most fully satisfied, and the thermal agitation to change the structure to one where the cohesive forces are less satisfied. Even in the gaseous films, the cohesive forces are to a very large extent satisfied, because the molecules are lying flat in contact with water along at least half of their area; this would be the case even with a perfectly gaseous film, and with the imperfectly gaseous films which actually occur there must be some satisfaction of affinities through chains adhering temporarily, while flat on the surface. From Harkins' measurements of interfacial adhesion, it appears that the attraction per unit area of hydrocarbon for water is about as great as that of hydrocarbon for hydrocarbon. The condensed films, however, give the fullest opportunity for satisfaction of the adhesional forces, since in the vertical, close-packed configuration alone are the chains in contact with other chains over their entire length. Hence rise of temperature changes condensed films into expanded, and finally into gaseous films.

*Attraction of End Groups for Water.*—Langmuir first pointed out the importance of the end group in anchoring the molecule to the water. Unless an end group with a considerable attraction for water is present, the films of long chain substances cannot be formed, or are very unstable and collapse rapidly. It is possible to distinguish the attraction of end groups for water by noting the tendency of the films to collapse. The hydrocarbons, and alkyl halides, cannot be induced to form films on water; the ethers and phenol ethers form transient films when spread by a solvent; the methyl esters show slight signs of collapse, while the acids and many other series of compounds form films which will usually resist 10 dynes per cm. compression, or more, with very little collapse. 10 dynes per cm. is a compression, on these very thin films, of the order 40 atmospheres. The adhesion between the ends of the molecules and the water must be very great to prevent buckling of the films under this, or larger, compressions.

The following is a rough classification of the intensity of the attraction of end groups for water, based on qualitative observations of stability made incidentally to the study of the structure of the films:—

(A) Very weak attraction, no film formed:—Hydrocarbon,  $-\text{CH}_2\text{I}_2$ ,  $-\text{CH}_2\text{Br}$ ,  $-\text{CH}_2\text{Cl}$ .

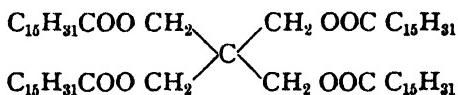
(B) Weak attraction, films unstable (groups in increasing order of attraction for water)  $-\text{CH}_2\text{OCH}_3$ ,  $-\text{C}_6\text{H}_4\text{OCH}_3$ ,  $-\text{COOCH}_3$ .

(C) Strong attraction.  $\text{CH}_2\text{OH}$ ,  $\text{COOH}$ ,  $\text{CN}$ ,  $\text{CONH}_2$ ,  $\text{CH}:\text{NOH}$ ,  $\text{C}_6\text{H}_4\text{OH}$ ,  $\text{CH}_2\text{COCH}_3$ .

This classification is in general agreement with the adhesions for water of liquids containing these groups. It requires further development as a method for comparing attractions. Cary and Rideal<sup>5</sup> have approached the problem from the other side, by examining the tendency of crystals floating on the surface to spread into films. They find that some of the films of class (C) are not thermodynamically stable, as the crystal will not always spread spontaneously at a temperature at which a film deposited by the aid of a volatile solvent is stable enough to examine at leisure. There is probably considerable passive resistance to attainment of equilibrium between film and crystal, especially from the side of the film, for as these authors suggest the film may tend to collapse into such an imperfect solid aggregate that its tendency to spread may be considerably greater than that of a perfectly formed crystal.

The tendency of films to collapse is not a simple function of the attraction of the end groups for water, but is a balance between the effect of the long chains which try to pull the molecules out of the films, and of the water attracting groups. The exact intensity of each must depend on the potential energies of molecules in film and in crystal. I have noticed however that films with very long chains always collapse more easily than those with chains of moderate length. Thus the methyl ester of the  $\text{C}_{34}$  acid, and the acetate of the  $\text{C}_{30}$  alcohol, collapsed readily; the corresponding esters of the  $\text{C}_{16}$  series gave stable films. The acid and alcohol of the  $\text{C}_{30}$  and  $\text{C}_{34}$  series were however stable. Crystals also have a lower tendency to spread, the greater the length of the chains.

Blocking the approach of the soluble group to water by a large group diminishes the stability of the films. Thus cetyl palmitate, palmitic anilide, benzyl and cyclohexyl palmitates do not form stable condensed films, though some of these compounds form moderately stable expanded or gaseous films; in these the molecules are flat and therefore the anchoring group can get near the water. With pentaerythritol tetrapalmitate



a fairly stable film is formed. If the molecule retained its symmetrical structure on the surface, the oxygenated groups could not get near the water. It forms a condensed film, however, with all four chains vertical, so that the cohesional forces here distort the molecule so as to obtain the most stable film. The molecule is of course not one that would offer much resistance to distortion in this manner.

*Melting-Points of Crystals and Intermolecular Attractions.*—Since the intermolecular forces operating in the films are the same as those holding matter together in crystals, a correlation must exist between the properties of crystals and the intermolecular forces as discovered from the films. In the crystals of the fatty acids, the long chains lie side by side in sheets, probably inclined to the normal to the sheets, and the sheets are double

layers with the oxygenated group of the molecules on each side turned towards the oxygenated groups of the other side. The melting-points of the series of fatty acids and their esters are what would be expected from their structure and the knowledge that the principal stabilising forces are the attractions of the long chains to each other and of the oxygenated groups to other oxygenated groups.

Thus, except for the slight alternating effect between odd and even acids, which is due to a peculiar packing of the COOH groups, the melting-points rise with increasing length of chain up to 22 carbon atoms. This is parallel to the increase of expansion temperature in the films with increasing length of chain. Again, the length of chain being kept constant, the melting-point drops very rapidly on esterifying the COOH group. In the palmitic series, the acid melts at 62.5°, the methyl ester at 30°, the propyl at 15°, the iso-amyl at 12°.

This shows the rapid impairment of the adhesion between the oxygenated groups, which binds the two halves of the sheets together. Even the small methyl group is sufficient to diminish the adhesion by more than half the maximum diminution caused by the amyl group. As the alcoholic chain is further lengthened, the melting-point begins to rise again. Octyl is 25°, dodecyl 41°, hexadecyl 53°, octadecyl 59°. Here, as the X-ray investigations show, the long alcoholic chains lie side by side and their increasing length confers increasing stability on the structure, the tendency of the oxygenated groups to bind the monomolecular layers together in pairs being now entirely overcome by the large groups blocking them. That these two forces, the lateral adhesion of chains and the adhesion of oxygenated groups are the most important cohesive forces in the crystal is shown by the fact that it was possible to predict the crystal structure of the long chain substances correctly from the assumption of these forces and the melting-point relationships just mentioned, except for the details of tilt of the molecules and of the packing of the COOH group which causes the alternation between odd and even acids.

Other homologous series may be treated in the same way; with a little experience it is possible to acquire some skill in the prediction of the melting-points of long chain compounds, and it may soon be possible to attempt a systematic classification of organic groupings according to the stability of their adhesions in the crystal.

Some progress has been made, in mapping the broad outlines of the attractive forces round molecules, and of the repulsive forces commonly known as the "shapes" of the molecules. We now know that the structural formulae of Organic Chemistry, too often taught as being merely symbolic representations of reactions, do in fact represent the shapes of the molecules with considerable accuracy. It will be a long time, however, before the really fine details of shape and attractive forces near to individual atoms are known in sufficient detail to say why one film is solid and packs with heads in contact and chains tilted, and another is liquid although the chains are vertical and as closely packed as possible. To discover this will need investigation along many lines, and the combination of knowledge gained from studies on the shapes, thermal properties and crystalline structure of matter in many forms. It is satisfactory to know that such studies are being systematically and successfully pursued.

# A NOTE ON COHESION IN THE CRYSTALLINE STATE.

By F. I. G. RAWLINS.

Received 14th October, 1927.

The purpose of this brief communication is to take stock of present-day knowledge in that domain of physics and physical chemistry which is concerned with the energetics of the crystalline state, and thus ultimately with the fact of continued existence—shortly the permanence—of matter in the solid form. Rapid progress in what Goldschmidt<sup>1</sup> and his followers call crystal construction has brought to light some fascinating suggestions as to how, from a knowledge of ionic magnitudes, deformation and so forth, it is possible to build up a crystal having nearly any desired property—at least within wide limits. Not content with this, he is able to provide “crystal models” in the sense that natural complexes can be prepared having all the properties of the prototype though on a reduced scale of linear dimensions, or with some other characteristic increased or reduced by a constant factor.

As it happens, these advances have been roughly contemporaneous with the advent of the new wave mechanics associated with the names of de Broglie and Schrödinger: the time may therefore be opportune to examine in outline the possibilities lying ahead of “explaining” some of the remarkable empirical results above indicated.

Probably<sup>2</sup> it is hardly necessary to labour the point of the ultimate electrical nature of the forces of cohesion in crystals; it will be more profitable to discuss at once a few types of crystal lattice offering attractive problems in cohesion.

Pauling<sup>3</sup> has recently dealt with the conceptions of the new mechanics in so far as they influence our understanding of ionic, or heteropolar, crystals. In a word, the two demands that the wave-function  $\psi$  should be single-valued and everywhere finite supersedes all the older rules of quantisation. The atomic or ionic sphere is thus infinite in extent—though the effective electric density is comprised within a distance of a few angstroms from the nucleus—i.e., it corresponds in order of magnitude with the “size” of an atom or ion on the earlier Böhr-Sommerfeld scheme.

It is no longer assumed that the inter-atomic repulsive forces in crystals have their seat in deviations from spherical symmetry, i.e., the interaction of poles of high order: from what has just been said, repulsion is the result of atomic inter-penetration. In addition, it appears that the calculation of a number of characteristic screening constants permits the establishment of a potential function—albeit somewhat complicated—for simple binary compounds. The Coulomb energy remains as before, but the potential of the repulsive forces is exponential in character instead of the inverse  $n$ th power of the distance as has been usually applied hitherto. Discrimination between these two alternatives need not concern us here: it will be sufficient

<sup>1</sup> Goldschmidt, *Z. tech. Physik*, 1927, 8, 25; *Ber.*, 1927, 60, 1263.

<sup>2</sup> For a general discussion without the new mechanics see Geiger-Scheel “Handbuch,” Vols. X. and XXIV.

<sup>3</sup> Pauling, *J. Amer. Chem. Soc.*, 1927, 49, 765.

to remark that a difference of some 2000 calories per mol. results for the lattice energies in crystals of the NaCl type. The hope may be expressed that this will lead to the performance of experiments of greater refinement in this direction.

In addition to the part played by ionic radii in determining the nature of the lattice which given compounds will form in the crystalline state, Goldschmidt<sup>1</sup> has discussed, from an empirical viewpoint, the influence of ionic deformability, *i.e.*, the term  $\alpha$  in Born's work, the electric moment per unit field. Hund<sup>4</sup> has discussed this problem theoretically with special reference to molecular and "stratified" lattices. ("Stratified" is suggested as a tolerable translation of "schichten" under the circumstances; the term will probably become important in future work.) These special lattices are invariably associated with great ionic deformability, and usually with large differences between the ionic radii of the constituents.

In a molecular lattice (*e.g.*, solid CO<sub>2</sub>, solid HCl, and just possibly LiI) the linkage is presumably heteropolar within the molecule, and homopolar as between molecule and molecule. Some such view as this would account in a general way for the properties of HCl: the gas is, almost without doubt, a perfect polar molecule, but a number of facts lead one to the conviction that solid HCl is very different from a typical ionic salt—a state of affairs due to the persistence of polar properties within the molecule, modified by homopolar linkages as between one molecule and another in the solid crystal.

It should be borne in mind that the effective moment of a diatomic molecule is usually some 20 per cent. less in the gaseous state than in the crystal. A systematic investigation of properties connected with cohesion in crystals having a molecular lattice (*e.g.*, compressibilities and elastic constants) offers an ambitious but attractive problem.

The paramount need is a recognition of privileged directions in such cases, since it is of no avail to obtain a series of mean values as is generally all that is accomplished. This becomes even more obvious for stratified lattices, which it is now intended to discuss.

Here the conditions requisite for stability—and, indeed, for the formation of such a lattice at all are, generally speaking, a molecule of the chemical form AB<sub>2</sub> composed of ions, one of which is much more easily deformable than the other: a perfect example is the hexagonal crystal cadmium iodide CdI<sub>2</sub>,<sup>6</sup> in which the comparatively rigid cadmium is bordered on either side by the easily polarisable iodine, the whole being a series of layers—hence the name—any one of which might be conceived as a vast neutral molecule.

Forces of great magnitude, perhaps even pseudo-heteropolar, must be operative within each layer, whereas the weakest of forces akin to homopolar hold the layers together. Actually, the crystal forms beautiful flakes, giving evidence of its stratified habit.

A number of other considerations affecting metalloidal and truly metallic crystals have been discussed by Goldschmidt<sup>1</sup> and by Friederich.<sup>6</sup> Probably other speakers at the present symposium will deal with them. The purpose of the present review has been to suggest that the nature of cohesion in special crystal lattices may be sought in a combination of the theories valid for truly heteropolar and truly homopolar types.

<sup>4</sup>Hund, *Z. Physik*, 1925, 34, 833.

<sup>5</sup>Bozorth, *J. Amer. Chem. Soc.*, 1922, 44, 2232.

<sup>6</sup>*Z. Physik*, 1925, 31, 813

# SOME PROPERTIES OF NON-METALLIC ELEMENTS. IN RELATION TO THEIR COHESIVE FORCES.

By A. M. TAYLOR, RAMSAY MEMORIAL RESEARCH FELLOW.

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1. Cohesion may be explained in terms of the attractive forces operating between unlike charges, and between electric doublets. For brevity the following classification may be adopted :

TABLE I.

	Linkage.	Origin of Cohesive Force.
Non-metals	homopolar	Electric doublets (arising from deformation).
Polar salts	heteropolar	Ionic charges + Electric doublets.

The electric doublets are produced under the influence of an electric field of intensity  $E$  by deformation of the electronic shell surrounding each atomic nucleus, and have a moment  $p$  where  $p = aE$ . (The constant  $a$  may be found by measurement of the atomic refractivity, or from the correction of the Rydberg number in the formula for the series spectra of the element.)

Thus it would appear that the cohesive force  $F_c$  acting across any plane in a solid<sup>1</sup> is given by the sum of the electrostatic forces  $F_e(r)$  due to charges, and  $F_p(r)$  due to electric doublets, so that

$$F_c = \Sigma F_e(r) + \Sigma F_p(r) - \Sigma F_R(r)$$

where  $r$  is a crystal parameter of length, and the term  $F_R(r)$  is the repulsive force due to mutual interaction of the electronic shells.

2. In polar crystal lattices the units are oppositely charged ions, and the forces of cohesion vary as the inverse square of the distance of separation, provided deformation of the electronic shells is absent. Since the effect of deformability is to set up electric doublets in the atoms and the attractive force between two doublets falls off as the inverse fourth power of the distance (which, as will be shown later, results in a greater value of the compressibility than when only the inverse square is concerned), increase in  $a$  is accompanied by increase in compressibility  $\kappa$ . Such an effect may be noticed in the following table :—

<sup>1</sup> Clearly the breaking tension of a crystal is given by the condition that  $F_c$  is a maximum, whereas the mean atomic volume is determined by the three conditions  $F_c = 0$  for each direction in space.

TABLE II.

	$\alpha$ (Halogen) in c.g.s. Units.	in c.g.s. Units.
KCl	$3.05 \times 10^{-24}$	$5.6 \times 10^{-12}$
KBr	$4.77$ "	$6.7$ "
KI	$6.28$ "	$8.6$ "

If some of the typical non-metals be examined both  $\alpha$  and  $\kappa$  are high :—

TABLE III.

	in c.g.s. Units.	in c.g.s. Units.	per $^{\circ}$ C.
S	$12.9 \times 10^{-12}$	$7.25 \times 10^{-24}$	$180 \times 10^{-6}$
Se	$11.8$ "	$6.4$ "	$150$ "
P (white)	$20.0$ "	—	$370$ "
Br	$5.8$ "	$4.17$ "	—
I	$13.0$ "	$6.28$ "	$250$ "

In the non-metals where the lattices are homopolar, the cohesive forces must be due solely to mutual attraction between the electric doublets, induced as a result of the high value of  $\alpha$ . It is natural that here the bulk modulus of compression should be low, since it will depend upon the differential of the force  $F$  between two doublets each of moment  $p$ ;  $F$  being given by

$$F = Cp^2/r^4 - \beta/r^n$$

where  $C$ ,  $\beta$  and  $n$  are constants. Differentiating, and eliminating  $\beta$  from the equilibrium condition ( $F = 0$ ,  $r = r_0$ ),

$$F' = -Cp^2(4 - n)/r^5 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The corresponding expression for polar compounds is

$$F' = -e^2(z - n)/r^3$$

where  $e$  is the charge on the ions; or re-writing,

$$F' = - (er)^2(z - n)/r^5 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From the foregoing it appears that  $F'$  in non-metals is smaller than the corresponding quantity in polar compounds, since  $p$  in equation (1) is small compared with  $(er)$  in equation (2), and the factor  $(4 - n)$  is numerically smaller than the corresponding term  $(z - n)$ . The high compressibility of non-metals is thus in accordance with expectation.

This quantity  $F'$  varies rapidly with  $r$ , much more so in non-metals than in polar compounds. In other words, the restoring force acting upon a displaced particle is, in non-metals, more markedly anharmonic than in salts, and consequently it will be anticipated that the thermal expansion  $\gamma$  will be high. This is seen from Table III. to be generally true. For comparison  $\gamma$  for the alkali halides is about  $120 \times 10^{-6}$  per  $^{\circ}$ C.

3. Broadly speaking, it may be stated that compressibility serves as an indication of the nature of the cohesive forces, whereas hardness may be treated as a qualitative estimate of their magnitude. When high values of

$\kappa$  are found in non-metallic elements—or in polar compounds—it may be conjectured that the units of which the crystal is composed are associated with considerable electric moment. The author<sup>2</sup> has so far been able to examine only the element sulphur in the infra-red spectrum, and so to demonstrate the existence of such an electric moment in the group S<sub>2</sub>; but as the cohesive forces in non-metals are due to attraction between the electric doublets associated with the elementary groups, it is to be hoped that methods will be devised for determining both the nature of the groups in other substances and also their electric moment.

<sup>2</sup> Taylor and Rideal, *Proc. Roy. Soc., A.* 115, p. 589, 1927.

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## COHESION AT SOLDERED SURFACES.

By T. B. CROW (JAMSHEDPUR, INDIA).

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A piece of metal with a soldered join in its middle may be considered (in regard to its cohesion as measured by mechanical tests), from two aspects, namely (1) as one compound piece of metal capable of resisting, as a whole, a certain stress, and (2) as a composite material (consisting of at least two *macroscopically* distinct members), whose breaking strength must be compared with the respective tenacities of the two constituent members. What will be the strength of a join, considered as a simple test piece, in terms of the strength of the solder in it? The ability of a soldered join, such as Fig. 1, to withstand rupture by a tensile force is evidently dependent upon the capacity of the solder to form a waist; *i.e.*, to flow: a possibility closely connected with the surface tensions operating at the interfaces with the copper. The same thing, of course, is true if a test bar be grooved as shown in Fig. 2; such a bar will "pull higher" than one of the same material not similarly grooved. Will fracture of the join take place in the body-metal, in the solder, or at an interface? Is there an interface, or does penetration of solder into body-metal or *vice versa* occur, so as to render definition poor or non-existent? What will be the variation of strength of a join with varying thickness of solder film, or with varying soldering temperatures, or with and without the application of pressure during joining? It was found that, with electrolytic copper rods and solder of eutectic composition:—

- (1) Decrease of gap width increased the tensile strength up to a

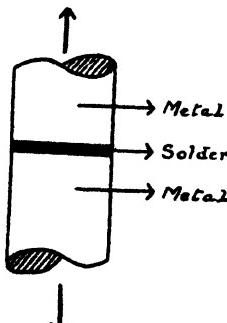


FIG. 1.

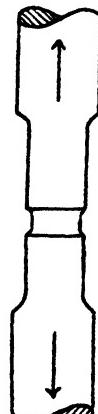


FIG. 2.

maximum of about 14 tons/inch<sup>2</sup>; after which further decrease in gap width (obtained by the agency of pressure), corresponded with a falling off in strength. In all these cases the solder used, when tested as solder, had a tensile strength of about 4 tons per sq. inch.

(2) The highest ultimate load of a join was always below the yield point of the copper.

(3) Elongation and yield points were observed only in those joins where there was a considerable thickness of solder in the gap; when the gap was 5·1 mm. (on a test piece having diameter of  $\frac{9}{16}$  in.) the test bar broke at a load about equal to that of ordinary eutectic solder.

(4) There was a certain temperature of soldering which gave a maximum strength, above which it rapidly fell off to about  $\frac{1}{3}$  of the maximum value.

(5) The microstructure of joins showed (a) the presence of an interfacial layer of copper-tin alloy (which is believed to correspond to Heycock and Neville's "H" constituent), between the copper and the solder, and (b) in joins made at higher temperature the development of a second phase,  $\eta$ , which appeared between the "H" and the mass of unchanged copper. These features are shown in Figs. 3 and 4, reproduced by kind permission of the Institute of Metals.

(6) In both classes of join (*i.e.*, those containing H only, or  $\eta$  plus H) fracture occurred in the region of the contact alloys on both sides of the central band of unchanged solder, through which the fracture also passed in steep cliff-like faces. The "high" and "low" levels thus formed each revealed two levels, which were of different shades. Thus in the case of "H" joins, fracture occurred both through the solder and through the contact-alloy H, in these contact-alloy regions as well as through the central solder mass as explained above. In the  $\eta + H$  joins, fracture occurred in the solder, the H, and the  $\eta$  in the contact-alloy regions as well as through the solder mass itself, as before. In both classes of join there is a possibility of the plane of fracture passing through an H-solder or an H - interface, though the adhesion between these (respective) materials may be and probably is, very great. Difficulty in ascertaining the exact course of fracture is largely due to the denticulated interfaces.

Where, as in the case of soldering copper in the experimental manner adopted by the author,<sup>1</sup> a relatively thick layer of a definite intermediate material, in the crystalline state, is obtained, explanations which reach no further than is implied by the expression intercrystalline cohesion or adhesion (whatever that may mean) might probably be sufficient. But where one expects to deal with layers which may be only a few molecules thick, and are possibly in the nature of an adsorbed product; or, when one encounters solid solutions formed by diffusion of one metal into the crystals of a body-metal, it is then that explanations of mechanism and strength of joins must be sought in terms of the electrical nature of cohesion forces. Ultimately, it should be possible to calculate the forces in operation from molecule to molecule in the interfacial regions of joins, and so verify the experimental values obtained and also to establish the theoretical course of fracture, which would naturally be across those regions having the weakest cohesive or adhesive bonds.

Two instances may be singled out for mention, in relation to joining of substances, illustrative of the widely different natures of the processes involved. Photo-micrographs of sections through glued joins of wood indicated that there is a running up of liquid glue between the fibres of the

<sup>1</sup> Trans. Farad. Soc., 58, XX., 1924; J. Inst. Met., XXXV., I., 1926, 55; J. Soc. Chem. Ind., 1924, XLIII., T., 65-70.

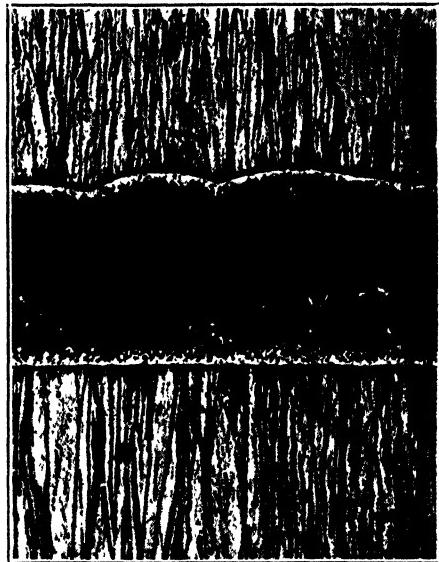


FIG. 3.—Showing solder, interfacial alloy "H" and unchanged copper. Magnification : 200. Polich attack followed by ammonium persulphate etch.

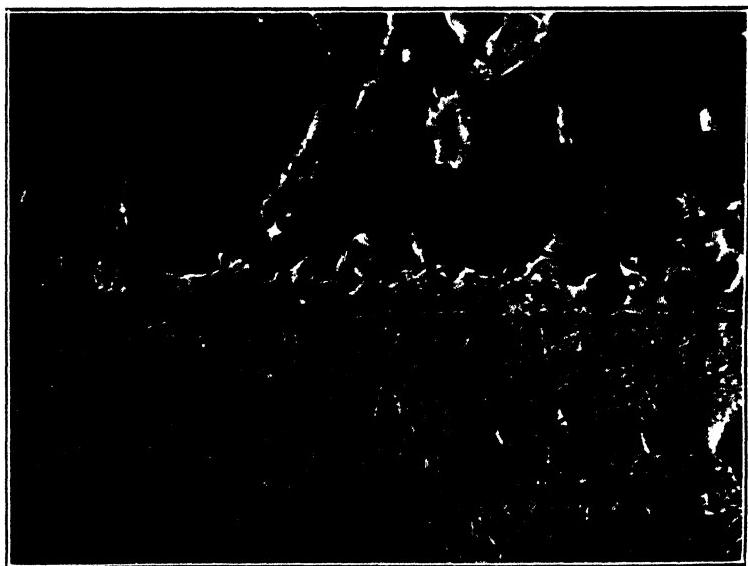


FIG. 4.—Showing one-half of join. Polygonal grains of copper (bottom); "η" constituent fringed with "H" constituent, solder (dark). "Islands" of "η," also fringed with "H" appear in the solder.  $\times 400$ . Etched with ammonium persulphate.

[To face page 160.]



wood by capillary attraction. Thus the glue, when solidified, is actually interlocked (by a series of hooks of itself) into the wood, and it is this which is largely responsible for the enormous strength of a properly glued job. Dickenson<sup>2</sup> and Miller<sup>3</sup> showed that molten solder could penetrate between crystals of certain alloys under certain conditions. Might not, then, an analogous series of solder hooks be formed between grains of body-metal. If this were so, grain size would have an important bearing upon the strength of joins. A further development on these lines arises from one of Hopkins conclusions that the strength of joins is a function of the properties of the body-metal, if the same adhesive be used to join different metals.

The other instance relates to the "cohesive-adhesion" of electro-deposited nickel upon steel, etc., when carried out under the special conditions devised by Mr. Fletcher, inventor of the "Fescol" process for building up, by deposition of nickel, worn parts of machinery. The essential features of Mr. Fletcher's process lie in the preliminary treatment which the basis metal receives by way of cleaning, and the conduct of the deposition process itself. Specially "built up" test bars were made and tested; in every case the bond of adhesion across the steel-nickel interface was stronger than the cohesion of the nickel itself, in which the fractures occurred. These observations caused Messrs. Heape and Grieg (*Trans. Faraday Soc.*) to incline to the belief that alloying was not an essential of a good soldered join.

One question to which attention should be drawn is the possibility of the use of different soldering fluxes giving use to joins of different strengths —other things being equal. The subject is too big to be detailed here, but what is wanted in this connection is some consideration of the properties of the actual surfaces of solderable metals when in a condition to "take" the solder. The behaviour of molten solder in contact with a solid metal is a particular instance of the general phenomena accompanying the contact of a liquid on a solid surface (and this solid surface, in the case of a metal about to be soldered, is in a certain condition, due to the action of a flux); the actual condition and molecular distribution of the applied solder or intermediary alloys a few molecules thick in the immediate region of the original body-metal surface (*i.e.*, what actually exists in the interfacial region, and how it got there) must be studied in the light of recent work of physicists on such questions as adsorption, activated surfaces, the nature of surfaces, etc., as instanced by the work of Devaux,<sup>4</sup> Langmuir,<sup>5</sup> Harkins,<sup>6</sup> Harkins and Cheng,<sup>7</sup> Bosanquet and Hartley,<sup>8</sup> and others.

### Summary.

Whatever the nature of cohesion and adhesion, the case of a soldered join (or, for that matter, many forms of joining or sticking phenomena) presents an exceedingly complicated instance of their action. In order to study cohesion and adhesion problems in joins, etc., it is necessary to find such a meaning to those terms as will enable them to be applied quantitatively to layers or films of materials which, in certain cases, might only be, at most a few molecules thick, and which were possibly in contact with other similar layers of different composition.

<sup>2</sup> *J. Inst. Metals*, 1920, **XXIV.**, 316.

<sup>3</sup> *Ibid.*, 1927, **XXXVII.**, 183.

<sup>4</sup> Devaux, *J. Physique et Radium*, **4**, 1923, 293.

<sup>5</sup> Langmuir, *Trans. Farad. Soc.*, **17**, 607, 654; *Trans. Farad. Soc.*, **15**, 62.

<sup>6</sup> Harkins, *Nat. Acad. Sci. Proc.*, **5**, 562.

<sup>7</sup> W. D. Harkins and Cheng, *J. Amer. Chem. Soc.*, **43**, 35.

<sup>8</sup> Bosanquet and Hartley, *Phil. Mag.*, **42**, 456.

# THE COLLOIDAL STATE AND COHESION AT THE TIME OF SOLIDIFICATION.

By JACQUES ERRÉRA.

*Received 23rd November, 1927.*

The hypothesis that certain bodies pass through a colloidal state of association during solidification, a condition which would remain persistent in the solid state in the neighbourhood of the point of fusion, seems justified.

Regarding this subject let me make the three following preliminary remarks :—

(1) In 1861 Thomas Graham<sup>1</sup> observed that the mechanical properties of ice in the neighbourhood of  $0^{\circ}$  were analogous to those of certain colloids. He compared the ice "to gum incompletely dried, to glue or any other firm jelly."

(2) Recently the experiments of Joffé<sup>2</sup> have shown that certain crystalline media, when we approach the point of fusion, are in a plastic state ; we can bend rods of rock-salt and change their form, and this plasticity can be compared with that of a colloidal medium. Joffé says that it is not impossible, according to his experiments of diffraction of the X-rays, that there are plastic layers between the solid structures. He therefore finds no argument against the hypothesis of passage through a colloidal state.

(3) The passage through a state of colloidal association between the liquid state and the solid, would be analogous to the similar well-known effect which occurs under certain conditions of temperature and pressure between the gaseous and the liquid states and which is characterised by the appearance of the critical opalescence.

The experiments we have made on the variations of the Dielectric Constant of certain media having permanent dipoles in the neighbourhood of the point of fusion, seem to us to favour the hypothesis put forward at the beginning.

Let us remember that the *D.C.* of a pure liquid having permanent dipoles is caused by the sum of the effects of polarisation of the electrons, atoms, and permanent molecular dipoles. The frequency of the current corresponding to the *D.C.* must be so low as to be less than the time of relaxation of the permanent dipoles and to allow them thus to follow the inversions of the current. For example, for water, the frequency must be less than about  $10^{11}$ . Recently we have shown that<sup>3</sup> if we solidify a medium having permanent dipoles and measure its *D.C.* at about  $10^{\circ}$  below the point of fusion and with a current of frequency higher than about  $10^6$ , we find that the *D.C.* of the solid is noticeably smaller than that of the liquid, as the permanent dipoles no longer act : they no longer contribute to polarisation. For example, for water the *D.C.* falls from 87 in the liquid state to 2·5 in the solid state ; for nitro-benzene, from 35 to 3·5 when we observe the conditions of frequency and of temperature indicated above.

<sup>1</sup> Thomas Graham works referred in Howard T. Barnes' paper in "Colloid Chemistry," edited by J. Alexander, 1926, p. 442.

<sup>2</sup> Joffé, *Report of the Physical Institute (Leningrad)*, 1926.

<sup>3</sup> Erréra, *Compt. Rend.*, 179, 155, 1924; *J. Physique*, 6, 304, 1924.

This lowering of the *D.C.* in solidification is quite general for media having permanent dipoles, and we have called the "*D.C.* proper of the solid" that which corresponds to the sum of the electronic and atomic polarisations, to the exclusion of the polarisations due to other constituents.

We have also shown that if we measure the *D.C.* of solids arising from liquids with permanent dipoles near the point of fusion and with frequencies inferior to  $10^6$ , we find values of the *D.C.* higher than the *D.C.* proper of the solid. The two full-line curves in Fig. 1 show the increase of the *D.C.* of solid acetic acid with lowering of frequency, this increase being less and less as we get farther away from the point of fusion. The dotted line gives this same dispersion of the *D.C.* of liquid acetic acid.

We, therefore, see that the *D.C.* of the solid can become higher than that of the liquid.

In order to make this fact clearer we give in Fig. 2 the variation of the *D.C.* of acetic acid with temperature at different frequencies. We see that for a frequency of 680 the *D.C.* during solidification jumps suddenly to a value of 18, and then drops within  $0.2^\circ\text{C}$ . to 8 when the *D.C.* of the liquid is 6.2.

We have found analogous facts for dimethyl sulphate, para-azoxyanisol and, taking the figures of the literature, for ice. The phenomenon is also produced at the moment of solidification when the liquid is supercooled. Other researches are being

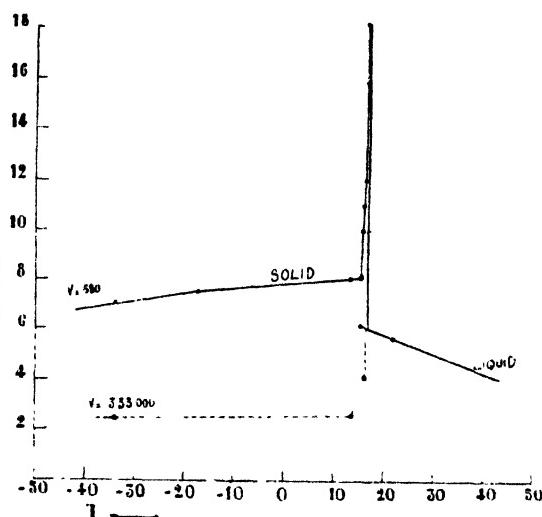


FIG. 1.

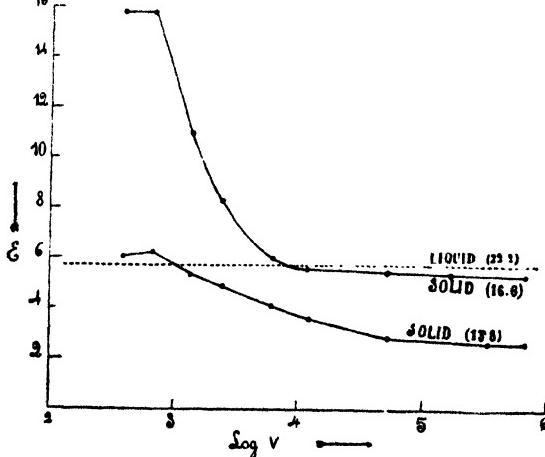


FIG. 2.

made at different frequencies in other media.

We suggest in explanation of this rise of *D.C.*, which exceeds that in the liquid state, that there is formation, at the moment of solidification, of

structures in a state of colloidal association. First it is to be noticed that this rise of *D.C.* is only found in media having permanent dipoles in the liquid state. It does not exist in media without permanent dipoles. We have made experiments on  $C_6H^6$ ,  $C_6H^{12}$ ,  $CCl^4$ ,  $TiCl^4$ ,  $SnCl^4$ , dichlorethylene, etc. The fact that there is no rise of *D.C.* for these media is no proof that they do not also pass through an associated state during solidification, but shows that the associated structures, if they are formed, have not a truly permanent electric moment.

On the other hand we know that liquids having permanent dipoles are associated and that, when the temperature falls, the association of these molecules increases. At the moment of solidification there would therefore be a sudden increase of this association. There would therefore be no discontinuity in the increase of association which accompanies the falling of the temperature, but, rather, a sudden increase during solidification. Thus, associated structures would be formed in such a manner that their dimensions would cause them to come under the category of media in the state of colloidal division, that is to say, of which the particles have a diameter between a few  $\mu\mu$  and about  $500 \mu\mu$ . Further, we must suppose that the arrangement of the molecular dipoles inside the colloidal structures is such that these last have a high electric moment, higher, indeed, than that of the molecular dipoles.

Indeed we see by the curves in Fig. 2 that when the frequency increases, the rise of *D.C.* which we believe to be due to the polarisation of the colloidal structures, becomes less and less, as if their time of relaxation were not reached. For high frequencies we find a continuous lowering of the *D.C.* during solidification, without the *D.C.* of the solid exceeding that of the liquid. These initial frequencies above which the rise of *D.C.* is produced to a noticeable degree at the time of solidification are of the same order as those which we have proved to be necessary to produce the rise of *D.C.* of certain colloidal solutions, such as the hydrocols of  $V^2O^5$  (of which the *D.C.* can reach the value of 1500), whose particles, which are rod shaped, have a high electric moment.

The substances considered, in passing from the liquid state to the solid, would pass through a state of colloidal association before arriving at the solid continuous state, as in the passage from the gaseous state to the liquid they can pass through a state where there are minute liquid drops having colloidal dimensions before arriving at the liquid continuous state. We suggest that these solid structures which, during their formation, pass through the state of colloidal association at the time of solidification, increase to such an extent as to result in structures having given dimensions by the plans of cleavage.

The absorption of electric energy which should accompany the rise of *D.C.*, consequent upon the fact that a new group of constitutive structures follows the reversals of current, cannot be demonstrated, owing to the sudden increase of resistance which accompanies solidification.

The hypothesis of the existence of colloidal structures in solids in the neighbourhood of the point of fusion is not inconsistent with that of the existence of free molecular dipoles in the solid. It rather verifies it in the case of media which are highly associated in the liquid state.

The experimental fact of the rise in *D.C.* is independent of the hypothesis of the existence of colloidal structures, but it seems to us at the present time that the latter explains the fact most adequately.

# COHESION AND RELATED PROBLEMS.

## GENERAL DISCUSSION

ON PAPERS PRESENTED TO THE SOCIETY ON 23RD NOVEMBER, 1927.<sup>1</sup>

**Professor B. P. Haigh** said that the paper contributed by Mr. H. J. Gough presented an admirable survey of recent experimental work on Plasticity and on Fatigue. Although the two subjects were naturally related, it appeared undesirable, in the opening paragraph, that Fatigue should be defined so broadly as to include all the phenomena exhibited by metals subjected to cyclic stress and strain : many of these phenomena, and particularly those of plasticity, were alike in cyclic loading and in static and were only indirectly related to fatigue failure.

Many of Mr. Gough's experiments appeared to him to illustrate the view that the safe range of stress is determined directly by the incidence of elastic hysteresis and only indirectly by plastic slip. It might have been hoped therefore that Mr. Gough would have given more attention to this view of the problem. But his statement, that elastic hysteresis and plastic slip are *both* operating when the safe stress is exceeded, might perhaps represent an advance on the earlier view, that "elastic hysteresis does not appear to be connected with failure under repeated stresses."<sup>2</sup>

The statement that the results of tests in media other than air must be taken into account, was to be welcomed as an important advance which had long been advocated and had already yielded valuable conclusions. The view that mechanical fatigue is determined directly by elastic hysteresis was originally based on a wide variety of experiments that included such tests, as well as others that were novel ; it was again considered in another paper contributed to this discussion. The earlier view, that fatigue failure is directly due to plastic slip, appeared to be fundamentally incompatible with the results of these investigations.

**Mr. H. J. Gough** said that Professor Haigh raised some extremely interesting points in connection with important aspects of fatigue ; as some of these points were illustrated by reference to his (Mr. Gough's) paper, he would attempt to clear up some of the questions raised. In the first place, exception was drawn to the very broad definition of the subject with which the paper opened. He could, however, see no alternative to the association of the terms "fatigue" and "cyclic stress or strain". The fact that static and fatigue failure presented so many points of similarity, was far from being undesirable, but surely pointed to the conclusion that the cause of the ultimate failure of cohesion was fundamentally the same in both types and, as a means of studying the main problem, fatigue failure presented many advantages, as the actual failure could be studied in as many stages as desired ; this no doubt accounted for the fact that the subject was receiving detailed study from many who were primarily interested in cohesion problems in general and only indirectly in the bearing of fatigue problems on engineering design.

<sup>1</sup> This volume pages 53 to 164.

<sup>2</sup> Gough and Hanson, *Proc. Roy. Soc., A.* 104, 563, 1923.

He was also entirely at a loss with regard to the meaning of Professor Haigh's statement that many of his experiments illustrated "the view that the safe range of stress is determined directly by the incidence of elastic hysteresis and only indirectly by plastic slip." The interpretation to be placed on the first part of this sentence was that only under an unsafe range of stress could a metal exhibit a state of elastic hysteresis. This, of course, was the view of the early experimenters. For example, Professor Ewing, in 1887, when describing his famous experiments on strain hysteresis, before the British Association, after pointing out that the metals used exhibited stress-strain relations which were represented by a closed loop of a definite area, concluded by remarking that "The result has a sufficiently obvious bearing on the conclusions of Wohler with regard to the deteriorating effects of repeated variations of stress." Since that time, a large number of accurate investigations had confirmed Ewing's observations of this state of quasi-elasticity and, moreover, had shown that the state can be observed under ranges of stress which are far removed below the limiting safe ranges of stress for particular metals investigated. He knew of no experiments that showed that "the safe range of stress is determined by the incidence of elastic hysteresis" (his own experiments showed precisely the opposite) and any such experiment would be directly contrary to the conclusions of a number of independent observers. These arguments could, of course, be set aside if the existence of a safe range of stress were denied, but he did not imagine that this represented Professor Haigh's view.

He felt that, possibly, some misunderstanding had arisen in regard to the exact meaning of Professor Haigh's remarks, and he therefore, took this opportunity of raising the matter.

With regard to the part played, in fatigue failure, by the effects of previous plastic slip, he considered that this was dealt with very fully in his paper, and did not require recapitulation. The single crystal experiments did indicate that hysteretic effects might be due in part to the stresses and strains set upon the crystal structure due to the residual effects of previous plastic slip. He also suggested, that in view of the intensive study now being given to fatigue problems, and of the new means of attack now available, it was above all things necessary to keep an entirely open mind about the fundamental causes of fatigue, in the hope that they might arrive ultimately at a state of knowledge which not only represented "an advance on earlier views" but might represent a state of exact knowledge.

**Mr. N. K. Adam** (*partly communicated later*) said that Professor Haigh's suggestion that a monomolecular film on a water surface might be obtained in tension was apparently supported by an observation very recently published by Langmuir.<sup>3</sup> A film of oleic acid, placed on the surface of an aqueous solution of ether, could be extended to an area some 20 per cent. greater than that at which the surface was just covered, and was shown to have no holes until it was punctured either by a glass rod or by pouring on a little ether vapour. This observation was made incidentally to an investigation of the effect of the films on the evaporation of water, and it appeared worth making a systematic search for conditions in which a film can be obtained in tension. Under the ordinary conditions of his (Mr. Adam's) experiments, the film did not transmit a tension; that might however be due to the film breaking away from its end supports rather than to a failure of the film itself.

It did not seem likely that any heat effect due to hysteresis cycles

<sup>3</sup> *J. physical Chem.*, 1927, 1730.

would be detectable in the films ; the heat capacity of the supporting water would probably mask any small thermal effects, which might occur in the monomolecular film.

**Sir William Bragg** said that he felt sure that the more intimate knowledge of the structure of solid bodies which X-ray analysis is supplying would lead to a better understanding of the cohesion problem : but he had no particular suggestion to make in this direction. The structural problem was being investigated on general lines ; this was the only way of making progress at present.

**Dr. H. J. Poole** said that he had been very interested in Professor Haigh's paper because some little time ago he (Dr. Poole) had made a study of the analogous and very pronounced phenomena in elastic jellies.

He noticed that Professor Haigh had criticised the use of the term Hysteresis on etymological grounds. He agreed, but since this misuse appeared to have the sanction of convention, he suggested that the term "Viscous Elastic Hysteresis" be employed to differentiate the effects of elastic afterworking and creep from that dealt with by Professor Haigh. This terminology would then be consistent with that of magnetic phenomena.

From the viewpoint of the instrument maker or the user of precision tools the question of creep and elastic after-working was, perhaps, more important than that of fatigue. He was surprised that this aspect of the

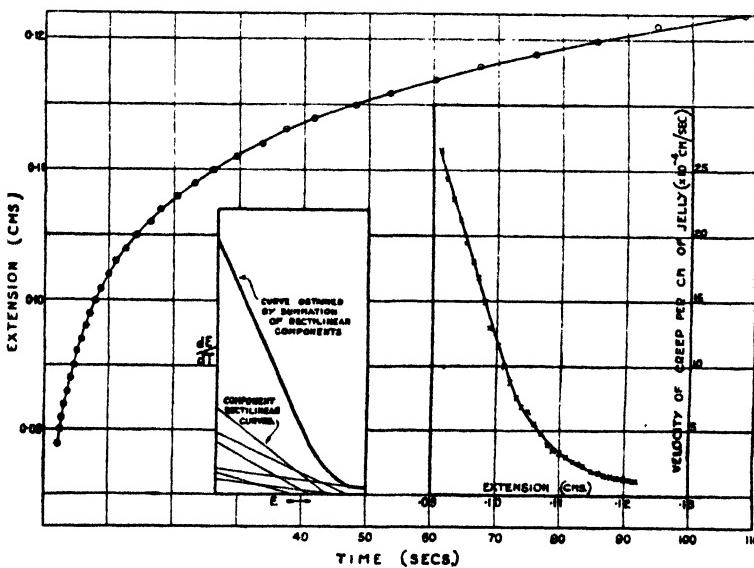


FIG. I.

subject had not been dealt with to any extent in the General Discussion. It might, for instance, prove of some importance when the results of high-speed fatigue tests were applied to slow cycles as, for example, in the design of bridges, rails, etc. Perhaps it might be of interest to recall the behaviour of jellies under stress.<sup>4</sup> A typical time-strain curve was shown in Fig. I. This curve was roughly exponential and suggested that it was derived from an equation of the type;

<sup>4</sup> Poole, *Trans. Farad. Soc.*, 21, 114, 1925; 22, 82, 1926.

$$K_1 E + K_2 d\eta E/dt = K_3$$

where  $E$  is the strain at any instant and  $\eta$  is the viscosity of the liquid phase. It would be seen from the inset curve that this relation was only observed during the early part of the extension. In actuality the elasticity of the framework and the viscosity of the liquid phase might vary from point to point in the structure so that the experimental curve was the resultant of several such equations all with different values of  $E$  and  $\eta$ . The result of this possibility was shown in the figure; the resultant curve was similar in shape to that obtained experimentally.

Dr. Poole said that not being a metallurgist, he could not say whether this explanation of the fact that a simple exponential did not agree with the results of similar experiments on metals might not, therefore, be new to those present. It might, however, serve to refocus attention upon this point particularly in view of the apparent plasticity of certain single crystals.

**Professor I. Masson** (*communicated later*) said that in view of Professor Lennard-Jones' and Miss Dent's stimulating analysis of cohesive forces, it should be useful to note evidence that was afforded by a study of the compressibility of gaseous mixtures.<sup>5</sup> Here it was proved experimentally that when two (non-polar) molecules attract each other, the force does not arise from any "chemical affinity" between the atoms in one molecule and the atoms in the other molecule. As one example: (i) A certain compressed mixture of argon with ethylene packed into a given volume under a pressure lower than it "ought to be" by as much as 8·5 per cent.; (ii) this was immediate evidence of a strong mutual cohesion between ethylene and the chemically inert argon;<sup>6</sup> (iii) the substitution of oxygen for the argon, in the mixtures with ethylene, made practically no difference in the figures obtained; (iv) hence the van der Waals' cohesion was no greater between oxygen and ethylene than between argon and ethylene, despite the expected affinity between  $O_2$  and  $C_2H_4$ .

In the light of this fact, care must be taken not to misinterpret Professor Desch's remark, "There is no essential difference between cohesive forces and those of chemical affinity." The difference between them could be rather more than one of degree only. For it was clear, from the above facts, that a pair of molecules could cohere without the slightest calling into play of the chemical affinity which, under other conditions, did manifest itself. This non-chemical—or van der Waals—type of cohesion was thus strictly molecular, whatever its origin; and its occurrence must be held to precede, and might be thought to give the occasion for, the exercise of the more intimate, close-range, inter-atomic types of cohesion, which constituted chemical affinity, and which were also exhibited between the polar substances studied by Hardy, Langmuir, Adam, and Sir W. Bragg's school.

A review of cases of adsorption such as that of low-pressure oxygen upon charcoal or upon tungsten, such as that of small amounts of water upon colloidal silica, and such as unimolecular films of oxygenated carbon-chain compounds upon glass or upon water, left little doubt that the mode of cohesion in all these cases was the same as in chemical co-ordination.

<sup>5</sup> Masson and Dolley, *Proc. Roy. Soc., A*, **103**, 524.

<sup>6</sup> The figure of 8·5 per cent. was purely experimental; and it became still greater if allowance were made, by calculation, for the pressure-effect due to the space available for one gas being restricted by the bodily bulk of the other. For this pressure-effect was such as to oppose the economy in pressure which mutual cohesion caused, and 8·5 per cent. was the nett resultant.

They might be classed as "chemical cohesion." Another interesting case of the same sort, but one in which the chemical cohesion was on a three-dimensional plan instead of on a surface, was in the hydration of zeolite crystals; and here it was incidentally worth noting that H. B. Baker showed in 1910 that water vapour will not pass through a naturally-anhydrous salt-crystal, but will pass through a crystal of a hydrated salt.

The simplest sequence which could be deduced from the facts as to the train of processes in which initially *neutral* molecules might be involved, was :—

$$\left\{ \begin{array}{l} \text{Free} \\ \text{molecules} \end{array} \right\} \rightleftharpoons \left\{ \begin{array}{l} \text{v. d. Waals'} \\ \text{cohesion} \end{array} \right\} \rightleftharpoons \left\{ \begin{array}{l} \text{molecular} \\ \text{co-ordination} \end{array} \right\} \rightarrow \left\{ \begin{array}{l} \text{interatomic} \\ \text{change} \end{array} \right\}.$$

This sequence might be briefly discussed.

In the paper referred to<sup>6</sup> the view was put forward that the molecular cohesion "between any two kinds of gas would primarily be no more than that of the gas or gases of the argon group whose electronic configurations they resemble." Professor Lennard-Jones had now crystallised this idea in a much more precise and more general form; for, starting from a similar hypothesis for ions and atoms in a solid, he had shown quantitatively how the forces referred to do stretch out beyond the range of ionic polar influences, although the latter transcend them at close quarters. Also he and Miss Dent had raised the interesting surmise that these outer attractive forces are caused by a mutual polarisation, set up as the two electronic systems approach one another. Here, in so far as both have an electronic origin, was the essential similarity between van der Waals' cohesion and chemical union. (If this notion were right, there was at least as much difference between van der Waals' cohesion and chemical cohesion or co-ordination, as between the latter and the polar union of ions; for co-valency or "electron-sharing" was evidently only a special case of electro-valency or electron-transfer.)

Apart from any hypothesis as to causes, however, it should be noted that the passage from van der Waals' adsorption to chemical adsorption, shown in the above scheme, was not a straightforward one. For (as Professor Lennard-Jones' theoretical studies of gaseous properties had shown with special precision) when one simple molecule approached another, they attracted each other with a force which began to be significant perhaps a dozen or more Angstrom units away, and rose to a maximum at a certain closeness of approach—several Angstrom units; but at still closer quarters, attraction ceased, and was suddenly outweighed by rapidly-mounting forces of repulsion. Even in ordinary gaseous collisions the zone of maximum attraction was passed through and the repulsive region was entered; and this remained true though the atoms of the colliding molecules were of kinds that could combine together chemically.

Hence the unaided van der Waals' cohesion, even at its maximum, was not only too weak to account for the tenacious adsorption of, e.g., low-pressure oxygen on charcoal, but it was even too weak to pin molecules together closely enough for their atoms to unite chemically. From the standpoint of adsorption of a gas on a solid, all that it could do was to increase slightly the frequency of kinetic encounters, and to build a very loose film.

It followed clearly that before two normal molecules, cohering together as by van der Waals, could proceed to the next stage, in which they cohered with that special intimacy that prevented the union being easily reversible,

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either or both of them must first undergo a change in electronic constitution ; and this change must be of a kind which they did not undergo in a simple kinetic encounter. It must be a change which partly abolished the repulsion that kept two normally-cohering molecules at a comparatively large distance apart. Mere duration of cohesion-contact seemed inadequate to account for such a change ; and so, apart from outside evidence, he was driven to interpose, in the middle of the above train of processes, some kind of activation of one or both molecules. Some extraneous supply of energy was needed, to bring about the necessary electronic dislocation. A perfect hydrated crystal was presumably capable of adsorbing vapours "physically" in some degree ; but, as was well known, it would not hydrate further in moist air (nor dehydrate in dry) until it was scratched. On the other hand, in amorphous and in cold-worked solids, and apparently in the intercrystalline "jam" of polycrystalline solids, the extra potential energy was already present, the atoms were already distorted and probably, even in a non-metal, highly polarised.<sup>7</sup> Accordingly, on substances, in that condition, the adsorption of neutral molecules could go past the loose, reversible, van der Waals' stage, in which attraction normally ceased within several Ångstrom units' distance, and could reach the stage of the really close adsorption resulting from the attractive fields having been brought to within one or two Ångstrom units from the atomic centres.

**Mr. A. Egerton** said that Professor Lennard-Jones' remarks interested him greatly, particularly the results relating to the Van der Waals' force. One could fully support his appeal for more data, particularly in regard to the behaviour of mixed gases at various temperatures, perhaps even in regions where the rate of chemical reaction is just beginning to become appreciable. He enquired whether it would be possible to evaluate theoretically, on the lines of the paper before the meeting, the value of the work done to remove a molecule of NaCl from the surface to infinity and, thereby, to obtain the latent heat of sublimation. Professor Lindemann pointed out some fourteen years ago, that the forces at the surface of a solid could be represented by a curve the resultant of the forces of attraction and repulsion and that

$$\int_{r_0}^{\infty} \frac{a}{r^m} dr - \int_{r_0}^{\infty} \frac{b}{r^n} dr = \lambda_0$$

where  $\lambda_0$  is the latent heat and  $m$  and  $n$  are the exponents of the attractive and repulsive forces with reference to the distance  $r$  between the molecules.

Then  $(m - 1)(n - 1)$  became  $\frac{2\pi^2 M r^2 r^2}{\lambda_0}$ . Applying this in the case of his (Mr. Egerton's) vapour pressure measurements of cadmium and zinc, the values for  $m$  and  $n$  worked out as the fourth and seventh power respectively for both metals. Although consideration of a power of a force of attraction and of repulsion in this way might not represent the actual state of affairs, it seemed to him that it might be possible that Professor Lennard-Jones could develop his calculations in some such manner, so that the latent heat and, hence, the vapour pressure of substances like NaCl might be calculated.

A phenomenon of considerable interest in connection with these discussions, was the mode of evaporation and condensation of metals ; the conditions at the surface were very important. A striking instance was the investigation of Volmer where it was found that mercury atoms reaching a

<sup>7</sup> Cf. also *Nature*, 19 Feb., 1927, pp. 267-269.

crystal surface of mercury did not condense where they struck but appeared to run along the surface and attach themselves to the edge of the growing crystal.

**Professor Lennard-Jones** said that the heat of sublimation of NaCl could be calculated by the methods of the paper, but it would be easier to use the relation  $S = U - V$ , where  $U$  is the energy of the crystal per gram molecule, and  $V$  is the energy of formation of one gram molecule of NaCl vapour from the ions of the metal and the halogen. Both  $U$  and  $V$  could be calculated from known interatomic forces.<sup>8</sup>

Professor Lennard-Jones referred to a statement made by Professor Joffé in his paper regarding the importance of cracks on the surface of rocksalt and their relation to the discrepancy between calculated and observed values of its tensile strength. The speaker said that it was possible to show theoretically that the interatomic distance of a single plane of rock-salt when isolated was less than that of the crystal in bulk. It followed that a considerable tangential force was set up at the surface and that this would no doubt cause cracking.

(Communicated later.) In view of the interesting analysis of cohesive forces suggested by Professor Masson from the chemical standpoint, it might be of interest to point out that an important step had recently been made on the theoretical side towards the understanding of the forces of chemical binding by Loudon, Heitten, and Suzaine.<sup>9</sup> These researches, based on the Schrödinger wave-mechanics and Paulis' "exclusion-principle," had thrown considerable light on the nature of the binding in homopolar molecules such as H<sub>2</sub>, even to the extent of giving quantitative determinations of the moment of inertia and heat of dissociation of H<sub>2</sub>. However, a corresponding theory of van der Waal forces had still to be worked out, so that the relation between these forces and the "chemical cohesive forces" still remained obscure.

He did not think that it was yet established that forces of the van der Waals' type were insufficient to explain any of the adsorption phenomena. As he and Miss Dent had shown in the appendix to their paper, such forces indicated a heat of adsorption of argon on KCl of about 2000 calories per gram molecule, which was of the order of magnitude of many observed heats of adsorption.

**Professor M. Polanyi**, referring to a remark of Professor Lennard-Jones about the influence of cracks on the tenacity of rock-salt, said that he thought that it had been shewn in a paper quoted in his contribution to the Discussion,<sup>10</sup> that the high tensile strength of rock-salt under water, which had been discovered by Joffé, was not due to the washing off of cracked surface. The following series of experiments, which had been made in collaboration with W. Ewald, proved, that a hardening by plastic flow was the real cause of this phenomenon :

- (1) Rock-salt, dry has a tensile strength of 0·5 kg./gm.
- (2) Rock-salt, wetted and then dried with alcohol and ether, has the same strength of 0·5 kg./gm.
- (3) Rock-salt in water has a heightened strength, which ranged in their experiments unto 5·0 kg./gm.

<sup>8</sup> Cf. Born and Heisenberg, *Z. Physik*, 23, 388 (1924), Lennard-Jones and Taylor *Roy. Soc. Proc. A.*, 109, 481 (1925).

<sup>9</sup> *Z. Physik*, 44, 455 (1927); 45, 484 (1927); 46, 455 (1928).

<sup>10</sup> *Z. Physik*, 28, 29 (1924) and 31, 776 (1925).

- (4) Rock-salt, that had been loaded under water to a stress up to 2·5 kg./gm., was dried with alcohol and ether and after this showed no loss of strength. A raising of the load was necessary to break it.

The cause of the hardening of rock-salt taking place under water, had been found to lie in an increased plasticity of wet rock-salt, compared with dry salt at equal loads. This had been proved by the following experiments :

Prisms of rock-salt were subjected to bending and the load was slowly raised. During the increase of load, the rock-salt prism was alternatively wetted and dried. In every wet phase a plastic flow was noted, which was immediately suppressed, either fully or for the greater part, when the prism was dried.

Unhappily there was to his knowledge no explanation for this increased plasticity.

Referring to the paper of Professor Taylor, he said that the boundaries of crystals had a distinctly increased resistance against deformation, even if the crystals were of cubic structure. This showed itself in the formation of ridges on the boundary lines, when aluminium rods composed of two or more large crystals were strained.

This phenomenon, of which as it seemed to him, no account was taken in the theory of Professor Taylor, played an important part in the effect of cold-working on microcrystalline material. It was due to the constraint on the grain boundaries that the homogeneous orientation of the crystals was broken up by cold-working, as shown by the disappearance of the contrast between reflections of the crystals and of the figures produced by etching. (Aetzfiguren.)

**Professor P. Ehrenfest** (*communicated*) said that the experiments mentioned by Professor Polanyi proved the (now undisputed) fact that plastic deformation increases the tensile strength. But he could not understand how Professor Polanyi obtained from these experiments any decision on the question as to whether the tensile strength or the elastic limit is influenced by the water.

The experiments of Joffé and his collaborators proved on the other hand, and so far as he, Professor Ehrenfest, could see, convincingly, that the elastic limit for the wet rock-salt is within 1 per cent., the same as for the dry salt.<sup>11</sup>

In addition, Joffé observed in the case of rock-salt under water a tensile strength *many hundred times* higher than in that of dry salt. Did Professor Polanyi wish to explain this *enormous increase* by the change of structure through plastic deformation ?

The beautiful "sphere experiment" of Joffé proved most clearly that it was the surface which was responsible for the normally enormous deficiency of tensile strength below the theoretical value. In that case, by an ingenious artifice he completely excluded any influence of the surface, so that the internal tensile strength reached in fact the order of magnitude expected by theory.<sup>12</sup>

The high dielectric strength described by Joffé in his paper presented to the meeting proved again, along independent lines, and very directly, the real existence of the high cohesion forces expected by the theory of Born,

<sup>11</sup> See especially Joffé and Lewitzky, *Z. Physik*, 31, 1925, where on p. 580 a discussion of the experiments of Polanyi is given.

<sup>12</sup> *Z. Physik*, 35, 442, 1926.

which were exactly of the order of magnitude measured first by Joffé in his experiments on the tensile strength of rock-salt and water.

**Dr. A. Müller**, referring to Professor Taylor's paper, said that the couple at the boundary of a crack would sooner or later destroy the continuity of the crystal lattice. Certain parts of the material would therefore differ in orientation from the rest.

In the case of simple slipping these dislocated parts of the material were likely to be small crystal particles which were rotated round a common direction. (The normal to the direction of slip in the slip plane.) This type of distortion could easily be identified by means of X-rays. It was actually found to exist in a sample of a stretched, single crystal of aluminium.

**Dr. C. J. Smithells** drew attention to a factor affecting cohesion which had not been referred to by other speakers, namely, the grain boundaries. Most metals when broken cold showed a fracture that passed through the crystals, rather than along the grain boundaries, but when broken at a sufficiently high temperature the fracture followed the grain boundaries rather than pass through a crystal. It appeared therefore that at low temperatures the cohesion across the grain boundary was greater than the cohesion between the planes in the crystal, but that this was reversed at higher temperatures. This indicated that the cohesion was of a different kind in the two cases; it would be interesting to have some theoretical explanation. It was of great practical importance in connection with creep at high temperatures. It had been shown in the case of tungsten filaments that resistance to sag or creep was intimately connected with the behaviour of the grain boundaries.<sup>13</sup>

A coiled filament in a lamp tended to sag under the action of gravity, but he and his co-workers had shown that this could only take place if there was a movement of the grain boundaries, and that the amount of creep was directly proportional to the change in grain size. If grain-growth could be prevented, either by the addition of thoria, which obstructs the movement of the boundaries, or by converting the filament into a single crystal, creep could be prevented. An understanding of the nature of cohesion between crystals might enable them to control the factors which determine creep at high temperatures. Their experiments indicated that the most creep-resisting structure was a single crystal.

**Professor A. W. Porter** enquired whether the equations given by Professor G. I. Taylor and others held good for anything but infinitesimal displacements.

In further explanation of the query, there could be no doubt of the application of the equations to infinitesimal changes starting from zero stresses. Also there was no doubt that the whole strain was the sum of infinitesimal strains. But being given that  $y = \int f dx$  and knowing  $f$  for very small values of  $x$  alone did not enable the integral to be obtained. There was necessary, further, a knowledge of  $f$  as a function of  $x$ . It was a knowledge of this factor which various contributors to the discussion had proposed to obtain by experiment and the curves of  $y$  against  $x$  represented their experimental results. There was as yet, however, no very clear explanation of these curves.

Professor Porter also drew attention to the necessity of allowing for the diminution of the cross-sectional area in calculating extension stresses. Unless this correction were made the load did not represent the stress. He did not see how any precise information leading to a true theory could

<sup>13</sup> Smithells, *Trans. Faraday Soc.*, 1921, 17, 485.

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be obtained otherwise. He reminded the meeting that in the investigations of Professor Andrade (to which allusion had already been made) the stress was automatically adjusted to constancy by means of hydrostatic compensation. The correction was specially necessary where there was very considerable viscous yielding.

**Mr. Robert Mond** submitted specimens of curved fibrous crystals of rock salt which he had found during his excavations at Luxor in Egypt, in certain underground passages and growing on the wall of a large hall, of which the ceiling had collapsed some three thousand years ago. The conditions of their formation appeared to be due to the very slow accretion from the gradual evaporation of the saline solutions dissolved out of the rock by the very rare rainfalls.

**Mr. D. Finlayson** suggested (with reference to the opening remarks of the President when he asked for suggestions for future research on the subject of this discussion), the necessity for some thorough work on the applications of the Quantum Theory to the problems of slip as affecting creep and fatigue.

To explain the very marked influence of a very small increment of stress on the "life" of a specimen in a creep or fatigue test, some time-recording mechanism must be imagined as existing in the specimen and responding selectively in some way to the applied stress. This mechanism they could only attribute to the effect of the vibrations of the atoms. They must assume, he thought, that at the absolute zero of temperature, the phenomena of creep and fatigue ceased to exist. If failure did not occur instantaneously, it could never occur, for there was no "clock" in existence to make one instant different from the next. He assumed that in this respect electronic movements were without influence.

Now, if they considered effects due to atomic vibrations, they must bring in the quantum theory; they knew from experience of theories of the specific heat of metals that no other method of treatment available at present was likely to prove equally serviceable. According to the quantum theory they must imagine that at any given temperature, the atoms were vibrating not with one definite frequency, but with a range of frequencies varying from zero to a maximum determined by the fact that the corresponding wave-length cannot be less than two atomic distances. On the basis of the existing theories the relative probabilities of each of these frequencies could be calculated, at least approximately. With the highest possible frequency, every two adjoining atoms were in opposite phase, i.e., swinging against each other; with lower frequencies two or more atoms in a row swung at any instant in the same direction; with very low frequencies thousands of atoms swung in this way. Now, the high frequency swings had small amplitudes, the low frequency swings large amplitudes, so that to explain qualitatively the influence of the applied stress on the rate of slip they had only to make the very natural assumption that the larger the stress, the smaller was the amplitude required in order to allow slip to occur. Various mechanisms capable of producing this result were readily pictured. A final choice between the different possibilities could be made more easily when sufficient data were available on which to test the conclusions.

Following this line of reasoning, they saw that when a number of atoms, say, in the plane of most favourable slip were moving along that plane in the same direction, they had, in effect, the equivalent of elastic waves moving through the atomic lattice in such a way that, in planes parallel to that just considered and at distances apart controlled by the reciprocal of

the frequency, they had series of other planes swinging with approximately the same amplitude in the same and in opposite directions. On this basis, they would expect slip bands to be approximately evenly spaced and close together when produced by a high stress, and far apart when produced by a low stress. Quantitative measurements correlating the width of spacing with the stress would be of interest. It therefore appeared unnecessary to assume, as some of the contributors to the Discussion had done, that there exist any planes of weakness in the crystal, or that metallic crystals are inherently imperfect.

It did not follow, however, from the above, that slip bands must inevitably be equally spaced; the superposition of large numbers of different frequencies must prevent anything more than a general tendency in this direction. Further, the suggestion was, that with any particular stress, slip can occur with all frequencies below a certain limit.

These considerations suggested a number of interesting consequences. The most obvious was the effect of temperature. The higher the temperature, the greater were the amplitudes of vibration and the more numerous the frequencies with which slip can occur. The suggestion that slip occurs in "waves," associated with "waves" at right angles, also made it easy to imagine an effect equivalent to a partial rotation about an axis perpendicular to the direction of slip, while the "unbalanced" effects of the high frequency oscillations during the moment of slip suggested a mechanism for the rumpling not only of the plane of slip but of numerous other planes in the vicinity, both perpendicular and parallel to that plane. It was obvious that whereas an oscillation can readily persist in a straight chain of atoms, it must be rapidly changed into oscillations in other directions in a rumpled chain. On these lines, there was, also, no great difficulty in picturing a mechanism capable of producing twinning.

The probability of the occurrence of a frequency below, or a wavelength above, certain limits must also depend on the boundary conditions of the crystal under consideration, since the wave on arriving at the crystal boundary must be partially reflected and partially transmitted according to the nature of the interlinkage of the two crystals and their relative lattice orientation. It was clear that the larger the crystal grain, the greater the chance of low frequency oscillations, and thus the greater the opportunity for slip under low stress. Thus each crystal might be conceived to have its own composite oscillation characteristics while the crystal boundaries served as media to preserve the dynamic equilibrium; in Professor Polanyi's words, the boundaries acted as constraints.

Professor Polanyi had pointed out that, whereas previously the failure of metals at stresses lower than the "theoretical" stress was attributed to accidental defects, the present tendency was to invoke the aid of thermal oscillations. The President had referred to the work of Tammann on those lines, and had suggested that one of the objections to the use of the Quantum Theory in this connection was that the frequencies to be considered were so low. It appeared to him, Mr. Finlayson, that the evidence was so clear that the influence of the thermal oscillations must be accepted, and that the necessity for a consideration of the low frequency oscillations must be boldly faced. The "theoretical" strength of a metal was merely its strength at the absolute zero. It might be recalled that the relatively high frequency vibrations constituting visible light were known for many years before the practical importance of the low frequency waves now used for wireless purposes was realised. Perhaps similar statements might yet be made about the high and low frequency oscillations existing in metals.

They had good reason to believe that the latter existed; they ought to examine closely their possible effects on the failure of metals.

In this connection it might be suggested that metallurgists have much to gain from a study of the quantum theory, whilst on the other hand, physicists engaged in the development of the quantum theory might find many useful suggestions in a study of the behaviour of metals under stress.

**Professor Perman** said that the adhesion of two portions of a crystalline substance was often caused by the formation of a crystalline film between them, e.g., when a block of ice is slapped against the wall of an "ice grotto," it sticks fast. He took this to be due to the freezing of a very thin film of water.

On the other hand, the very hard form of snow known as "wind board" was probably caused by the direct cohesion of snow crystals. It was formed at a low temperature from fresh snow lashed by a high wind; the crystals appeared to be broken down and rebuilt in a more compact form.

Again the caking of salts was often caused by the crystallisation of the salt from a film of solution between the crystals in contact. It was shown by Professor Lowry and himself that powdered ammonium nitrate would not cake if dried very thoroughly, but caked readily in the presence of a trace of moisture.

He should expect, however, any salt to cake under a high pressure, and he had shown that a mixture of sodium carbonate and barium sulphate forms a brittle coherent mass when thoroughly dried and then subjected to a pressure of 40 tons to the square inch, although no chemical action takes place.

**Professor E. N. da C. Andrade**, in commenting on the hardening of metals by deformation, referred to the remarkable experiments of Haussler and Scholz on single crystals. A copper rod, 16 mm. in diameter, which was a single crystal, could be bent in the hands like lead to begin with, but hardened with increasing deformation, so that it was very difficult to bend it into a semi-circle, and to bend it straight again would be beyond the powers of an athlete.

Referring to the President's remarks (p. 59) on the relative strength of the boundaries and the crystals themselves, he pointed out that he had been able to interpret his experiments on the flow of metals in terms of boundary and crystal flow. The flow, determined at constant stress by a special device, was analysed into two parts, one a part which rapidly diminished with time, and the other a part which was constant with time. The constant expressing the former reached a limit as the temperature and stress were increased, but the constant expressing the true viscous flow increased very rapidly with both stress and temperature. The former was therefore attributed to an effect taking place in the boundaries, while the latter was supposed to take place in the crystals themselves, which were known to become arch relation to the boundaries when the temperature was raised.

He also drew attention to the fact that it was not, as suggested by Professor Ehrenfest and others, an invariable fact that plastic deformation increased the tensile strength. With all pure metals with which the speaker had worked this was indeed the fact, but with a lead-tin alloy at  $-78^{\circ}\text{C}$ . a remarkable phenomenon was observed. If a wire of this material were extended at a certain stress constant there was very little immediate extension: the rate of increase of length had a small value to begin with, then increased, and finally diminished. That is, at a certain stage in the time history of the

heavily stressed wire the metal softened, but finally hardened and settled down to flow at a constant rate like a pure metal. Experiments at various stresses showed that the phenomenon was a genuine one, but the explanation was still to seek.

**Professor Polanyi** (*communicated later*), said with regard to Professor Ehrenfest's remarks that :—

(1) Since increase of cohesion arising from plastic flow had first been proved by the work on zinc done with Masing<sup>14</sup> showing an approximately hundredfold increase from 0·5-50 kg./mm.<sup>2</sup>, he confidently assumed that the greatest increase of cohesion observed by Joffé (estimated roughly as 300 fold—from 0·5-150 kg./mm.<sup>2</sup>) could be attributed to plastic flow.

(2) The "elastic limit" was at present an arbitrary value depending on the method of observation and could be depressed by using more refined methods, as was shown by the recent work of the Joffé school on rock salt.<sup>15</sup> In fact the stress value corresponding to any definite (small) degree of deformation could legitimately be taken as defining the "elastic limit."

(3) The real question, then, was whether or not the plastic flow curve was influenced by wetting, in the sense of easier flow. All workers were agreed that plastic flow of rock salt occurred at lower stress when wet than when dry.<sup>16</sup>

(4) Such an effect could not be explained by assuming an increase in the cohesion of rock salt in water; on the contrary, increased plasticity led to hardening and thence to increased cohesion. (The experiments quoted above proved this.) The same phenomenon occurred in the case of the effect of increased temperatures, which could increase cohesion by increasing plasticity, as shown by Joffé on rock salt and Sachs on zinc.

(5) He preferred to postpone discussion of Joffé's experiments on stress exerted in all directions on salt spheres till the promised calculations of Grunberg were available, and perhaps until it was known whether plastic deformation took place during the experiment. He, however, did not deny the possibility that cohesion under such stresses might be very much greater than under a tensile stress exerted in one direction only. In this connection, he recalled the remarkable observation of Voigt<sup>17</sup> that a rock salt prism was destroyed, under hydrostatic pressure, by the same load which would destroy it if it were not subjected to pressure, even though the pressure were so high as nearly to annihilate the tensile stress due to the load.

**The President** (Professor C. H. Desch), in summing up the discussion, wrote that the papers had brought together a number of modes of approaching a solution of the general problem of cohesion. A great step forward has been taken in the more accurate computation of the forces between atoms in a space lattice, and of their attractions on atoms in the neighbourhood, and although such calculations could only be made at present for lattices of the ionic type, it might be hoped that they would be later extended to the practically more important cases of metallic lattices, which presented greater difficulties owing to all the atoms bearing like charges. A remark by the writer in his survey, that chemical and cohesive forces were in all probability of the same kind, must not be taken as implying that simple exchange or sharing of electrons would account for all cohesive forces. It had emerged from the discussion that there had to be considered (a) inter-ionic forces as in the sodium chloride lattice, (b) forces due to the sharing

<sup>14</sup> *Erg. exakt. Naturwiss.*, 1923.

<sup>15</sup> Obreimow and Schutnikoff, *Z. Physik.*, 41, 907, 1927.

<sup>16</sup> Hentze, Ewald-Polanyi, Joffé-Lewitzky, *Ann. Physik.*, 53, 43, 1894.

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of electrons, as in organic compounds, (*c*) forces due to polarisation, as discussed by Professor Lennard-Jones, (*d*) the so-called Van der Waals' forces. The last were the least understood. It would seem that they were due to fields of force of a residual kind, and they probably played an important part in the formation of some classes of chemical compounds as well as in adsorption and similar phenomena on the border line between physical and chemical processes. In this respect, Professor Masson's remarks were very pertinent. The attraction between molecules of ethylene and argon could only be of a residual kind, but its magnitude was such as to be comparable with the other forces under consideration, and if such attractions could be manifested between chemically inert gases they were likely to be present in crystals, and to play an important part in the growth and reactions of crystals. There was still much difference of opinion as to the exponent of the force between atoms, whether attractive or repulsive, and that point must still be regarded as undecided.

It was unfortunate that no attempt had been made to examine the relation between the views of interatomic forces in the space lattice based on electrical theory, and the presentation of the subject by Professor Richards. The latter was based on observations of the compressibilities and other physical properties of solids, and it should be possible to reconcile the two methods of approach, especially since the deformation of atoms in contact with one another was now generally admitted. The study of intermetallic compounds undertaken by Mr. Hume-Rothery, now in course of publication, might be expected to help in this direction, by bridging the gap between polar salts and organic compounds on the one hand and mere solutions on the other. On the whole, it might be said that the fundamental question of the origin of cohesive forces was in a fair way to be solved.

Since the deformation of crystals proceeded by slip on closely packed atomic planes, it might be expected that a certain minimum shearing stress would be needed to overcome their adhesion. On the other hand, it had been definitely stated that single crystals had no range of primitive elasticity, giving measurable plastic deformation under a stress of  $0.1$  tons/in. This was, however, determined by means of an ordinary tensile testing machine, and it would be of interest to make further determinations by methods of greatly increased precision. Indications of a definite elastic limit had been found in single crystals of rock salt and zinc.

The deviation of observed strengths of solids from those calculated from electrical theory was very generally attributed to internal defects, but there was still much difference of opinion concerning the part played by cracks, as shown in the important discussion on the effect of water in allowing plastic deformation of crystals of rock salt.

As regarded hardening by cold work, although all the speakers were agreed as to an extensive disturbance of the space lattice, there was a wide disagreement as to the nature of that disturbance. It might be suggested that the hypothesis of Beilby, formerly so popular, was now unduly neglected, and that it deserved further consideration. Any hypothesis as to the nature of hardening must account for the diminution of density by cold-working, and also for the alteration in electrical and magnetic properties.

There was agreement as to the main facts of elastic hysteresis and fatigue, but some difference of opinion as to their interpretation. It had been established that the behaviour of single crystals towards alternating stresses did not differ in any important respect from that of aggregates, and that elastic hysteresis occurred in single crystals as well as in aggregates, with the same characteristic features, a cyclic state in which large amounts

of energy were dissipated continuing indefinitely. This fact simplified the problem, as it was no longer necessary to invoke the crystal boundary to account for the phenomenon. An interesting suggestion as to the nature of that boundary had been thrown out by Mr. Gough.

The influence of time on deformation called for much further study. Single crystals, when loaded in tension, showed creep during an appreciable time when the load was kept constant, but there did not appear to be any record of such creep continuing and increasing with time, as would be the case in true viscous flow. It would be of great interest to examine the behaviour of such crystals under constant load at high temperatures. Single crystal filaments of tungsten did not sag under load, but the properties of tungsten were in some respects exceptional, and it would not be safe to assume that all metals would behave similarly.

The fact that all slip planes of the same kind in a crystal did not take part simultaneously in deformation, but that slip occurred on a comparatively small number of planes at approximately equal distances apart, had been a stumbling block in the way of establishing a satisfactory theory. The suggestion made by Dr. Finlayson in the discussion, involving considerations of quanta, was deserving of full quantitative examination. Should it prove to be justified, it would help the interpretation of a whole group of facts in crystallography which were at present puzzling.

The Society was greatly indebted to the authors of papers and to those who had contributed to the discussion, particularly to their foreign guests, who had come long distances to assist. He believed that the bringing together of so much information, and the presentation of so many points of view by expert contributors, would be of great benefit to physics and to the study of the strength of materials.

## INDEX.

*Figures in heavy type against authors' names indicate personal contributions to the Discussion.*

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# THE KINETICS OF COAGULATION.

By B. N. DESAI.

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Within the last few years attempts have been made to derive an equation which will truly represent the changes which take place when an electrolyte is added to a sol. Smoluchowski<sup>1</sup> has proposed an equation to represent the kinetics of rapid coagulation on the assumptions that on the addition of an electrolyte (1) the potential of the micellae is instantaneously changed, (2) the charge on the miscellae is completely neutralised and hence there is no repulsive force opposing the coalescence, (3) the collisions are inelastic, i.e., every collision between the particles results in the formation of an aggregate.

Smoluchowski's equation for rapid coagulation has the form

$$\theta = \frac{I}{Kv_0} = \frac{I}{4\pi Drv_0} \quad \dots \quad \dots \quad \dots \quad \dots \quad (1)$$

where  $\theta$  is the specific coagulation time,  $K$  the velocity constant,  $v_0$  the number of particles at the beginning,  $r$  the radius of the sphere of attraction round each discharged particle, and  $I$  the diffusion coefficient.

This expression has been confirmed by Zsigmondy,<sup>2</sup> Westgren and Reitstötter,<sup>3</sup> and Krut and van Arkel.<sup>4</sup>

According to Smoluchowski<sup>1</sup> the slow coagulation can be distinguished from the rapid by the fact that in the former case all the encounters between the micellae are not effective, but only a proportion which depends upon the electrolyte concentration. Thus, the expression for slow coagulation will be

$$\theta_1 = \frac{I}{K_1 v_0} = \frac{I}{8\pi D rx v_0} \quad \dots \quad \dots \quad \dots \quad \dots \quad (2)$$

where  $x$  is the fraction by which  $K$ , the velocity constant for rapid coagulation, must be multiplied. If this theory is correct, we should be able to pass from a coagulation velocity curve of rapid coagulation to one of slow coagulation at a lower electrolyte concentration by multiplying the times  $t$  by a certain numerical factor, i.e. the curves of coagulation velocity must be related to one another. This expression for slow coagulation has been confirmed by Westgren.<sup>5</sup> Mukherjee,<sup>6</sup> on the other hand, has shown that it is valid only up to a certain stage of coalescence.

<sup>1</sup> *Physikal Z.*, 1916, 17, 557, 583; *Z. physik. Chem.*, 1917, 92, 129.

<sup>2</sup> *Ibid.*, 1918, 92, 600.

<sup>3</sup> *Ibid.*, 1918, 92, 750.

<sup>4</sup> *Rec. Trav. Chim.*, 1920, 39, 656.

<sup>5</sup> *Ark. Matem. Astron. Fys.*, 1918, 13, 14.

<sup>6</sup> *J. Chem. Soc.*, 1924, 125, 794.

Miyazawa,<sup>7</sup> Ishizaka,<sup>8</sup> Paine,<sup>9</sup> Gann,<sup>10</sup> Lottermoser,<sup>11</sup> Weigner,<sup>12</sup> and Galecki<sup>13</sup> have shown that the rate of coagulation over the sensitive range of electrolyte concentration may not be a simple reaction, as postulated by Smoluchowski. According to them, the rate of slow coagulation has an autocatalytic character and the reaction velocity can be represented by the equation :—

$$\frac{dx}{dt} = K(1 + bx)(1 - x) \dots \dots \dots \quad (3)$$

where  $K$  and  $b$  are constants and  $x$  the amount of change in time  $t$ .

The purpose of this investigation is to test the validity of the above two theories of the kinetics of coagulation by a very accurate method.

### Methods of following the Course of Coagulation.

Various methods have been used to follow the course of coagulation, but none of them has proved to be free from all defects.

Paine<sup>9</sup> has determined the velocity of coagulation of a copper (or copper oxide) sol by electrolytes by estimating the amount of uncoagulated copper at different intervals. He separated the coagulated coarser particles from the uncoagulated ones by stirring, dissolved the uncoagulated copper by adding a known amount of nitric acid and then estimated the excess of the acid. The defect of the method lies in the fact that while stirring has an extremely small effect in the beginning on the already coagulated but still small particles of the amicronic and submicronic size, it might affect them to a very high degree as soon as they have become considerably larger in course of time. Therefore, it is possible that the apparent autocatalytic course observed by Paine might have been due to this stirring effect.

Miyazawa,<sup>7</sup> Ishizaka,<sup>8</sup> and Gann<sup>10</sup> have followed the coagulation velocity by observing the change in viscosity of the sol. Now, as the viscosity depends upon the total volume of the particles, alteration of the "hydration" of the colloid particles might affect the viscosity measurements, especially in the later stages of coagulation.<sup>14</sup> Therefore, in the later measurements of viscosity a considerable increase might be found due to this hydration effect, and hence the apparent autocatalytic nature of the reaction.

Zsigmondy<sup>2</sup> and Kruyt and van Arkel<sup>4</sup> have followed the changes in a sol after addition of the electrolyte by means of an ultramicroscope. Undoubtedly, this is one of the best methods as the decrease in the number of particles is directly observed, but the method has its own drawbacks. First, very dilute sols have to be used in order to count the number of particles successfully and, therefore, it is possible that the autocatalytic nature of the reaction might not be observed. This can be observed markedly in fairly concentrated sols which contain a considerably larger number of particles, because sufficiently large multiple particles can be formed in them. Secondly, the walls of the cell containing the colloid might have also some effect on the course of the reaction. There is a possibility of greater percentage error with dilute sols—which alone can be used with this method—than with concentrated ones, owing to this effect. Thirdly, the particles of amicronic size

<sup>7</sup> *J.C.S. Tokio*, 1912, 33, 1179.

<sup>8</sup> *Z. physik. Chem.*, 1913, 83, 97.

<sup>9</sup> *Kolloidchem. Beih.*, 1912, 4, 24.

<sup>10</sup> *Koll. Z.*, 1914, 15, 145.

<sup>11</sup> *Z. anorg. Chem.*, 1912, 74, 174.

<sup>12</sup> *Ibid.*, 1916, 8, 65.

<sup>13</sup> *Ibid.*, 1911, 8, 227.

<sup>14</sup> Freundlich, *Colloid and Capillary Chemistry*, 1922, 440.

will not at first be visible, but make their appearance suddenly in the later stages of coagulation when they reach submicronic size. Fourthly, a sufficient number of readings might not be obtained for each experiment, because of the limited number of particles studied.

Hatschek<sup>16</sup> has developed the wedge method for gold sols in which colour changes in the coagulating sol are compared with the standard red and blue from time to time. The percentage of red remaining gives the amount of the uncoagulated sol. The method seems to be very simple and easy to carry out, but it is limited to gold sols where the colour changes are very marked. Moreover, the assumption that the red colour is due to primaries requires that all the particles in the sol must be of the same size. It is well known that gold sols contain particles varying from amicronic to submicronic size. If this be the case, the amicrons are sure to play an important part in the later stages of coagulation and might be taken as showing the absence of the autocatalytic nature of the reaction. It is, however, possible to prepare gold sols containing particles of fairly uniform size by the methods developed by Zsigmondy and others, but the fact remains that the above-mentioned defect ought to be taken into consideration. Again, the human eye may make considerable error in comparing the colour of the coagulated sol with the standards.

Mukherjee and Papaconstantinou<sup>16</sup> have measured the coagulation velocity of gold sols spectrophotometrically. They have also utilised the colour change in the coagulating sol as their criterion in calculating the coagulation velocity from the spectrophotometric measurements. The method though very accurate is subject to the same criticism as the Hatschek wedge method, so far as the assumption that the red colour of the sol is due to the primaries alone is concerned. Moreover, the method can be used only to follow the changes in the coagulating sol from the range—red to blue and is not applicable when the limit of absorption has been reached. This is an important point which must be borne in mind while estimating the exactness of the method.

The velocity of coagulation may be best studied by utilising a property which varies only with the increase in the size of the particles. Such a property is the scattering of light by the particles, which is directly proportional to their size. Therefore, the intensity of the transmitted light will decrease with the increase in the size of the particles. The use of this property in measuring the rate of coagulation has one fundamental advantage, in that it reveals the properties of the dispersed phase without disturbing its delicate equilibrium. The intensity of the transmitted light can be measured under suitable conditions, with the least possible difficulty, very accurately. In fact this property—the scattering of light—is so characteristic and extremely sensitive that it has been applied with success to the study of gaseous systems.

Mukherjee and Majumdar<sup>17</sup> have utilised this property to measure the velocity of coagulation of an arsenious sulphide sol when coagulators are added to it. The light from a source was allowed to pass through the cell containing the colloid + electrolyte and the intensity of the transmitted light was measured by allowing it to fall on a very sensitive thermopile connected with a galvanometer, which gave a deflection proportional to the intensity of the transmitted light falling on the thermopile. Unfortunately, adequate provision was not made to cope with all the difficulties that are likely to

<sup>15</sup> *Trans. Faraday Soc.*, 1921, 17, 499.

<sup>16</sup> *J. Chem. Soc.*, 1920, 117, 1563.

<sup>17</sup> *Ibid.*, 1924, 125, 794.

arise and, therefore, the initial slow coagulation phenomena, which have been observed even with not very refined methods, seem to have escaped their notice. First, they overlooked the fact that the colour of the arsenious sulphide particles might vary with the increase in their size, although Mukherjee and Papaconstantinou<sup>16</sup> used this very property to follow the course of coagulation of gold sols. Thus it will be seen that there is a probability of error in their measurements. Such an error can easily be obviated by using a suitable colour filter which will from the beginning cut off, before it passes through the cell containing the reaction mixture, the light of all wave-lengths which might be absorbed most by the coagulated particles during the increase in their size. Such an error seems to have been partly responsible for the non-observance of the initial slow coagulation velocity, because of the probability of the transmitted light having been deprived of some waves by absorption by the larger coagulated particles. Such a secondary effect seems to be the cause of a comparatively greater initial decrease in deflection.

Further, Freundlich and Nathansohn<sup>18</sup> have investigated the effect of light on arsenious sulphide sol. According to them, the sol becomes turbid when exposed to a Nitra lamp and its flocculation value by electrolytes is lowered. The same thing has also been observed by the writer. A sample of arsenious sulphide sol when exposed to sunlight for five to ten minutes became turbid, with a simultaneous change in colour. It seems that a complex sulphide compound is formed because of this photochemical change, with simultaneous formation of fine colloidal sulphur. In the light of these facts, it is very probable that, in the beginning of the process of coalescence, the galvanometer deflection observed by Mukherjee and Majumdar<sup>17</sup> was larger than that due solely to the action of the added electrolyte and, therefore, they could note the initial slow coagulation phenomenon.

It is preferable to use a photo-electric cell rather than a thermopile, for the former is decidedly more sensitive and reliable, as it is much easier to eliminate stray light than stray heat which may be emitted from all parts of the apparatus. Objections have, however, frequently been raised to photo-electric cells on the score of short life, fragility and change of sensitivity, but experience has proved otherwise. The cell used by Dobson, Griffith, and Harrison<sup>19</sup> though employed for nearly eight years was in perfect working order, although no special precaution was taken. Moreover, it is now possible to get photoelectric cells of great reliability and accuracy and, therefore, there are no grounds for the above criticisms.

Lottermoser<sup>11</sup> seems to have used a photoelectric cell to measure the velocity of coagulation of tungstic acid sol. However, he used the method in its crude form and at a time when the cells were not very reliable; consequently it has not received due attention from workers in the field. Freundlich<sup>14</sup> has, however, criticised the method as follows: "The possibility exists, however, that as in the case of increase in viscosity, the larger flakes appearing in the later stages of coagulation exert a stronger influence upon the appearance than the double and triple particles at first formed." Assuming, however, that the particles are hydrated, there is no possibility that the measurements will be affected in the same manner as the viscosity of the sol. The amount of transmitted light will not be reduced by surrounding the particles with a water envelope. It is well known that dust-free water does not scatter light to

<sup>18</sup> *Kolloid Z.* **28**, 1921, 258.

<sup>19</sup> *Photographic Photometry*, 1926, 61 f.

an appreciable extent and, therefore, the effect on the transmitted light of the water envelope round the colloid particle will be the same as if it had to pass through dust-free water.<sup>20</sup> The scattering of the light will be only proportional, in the circumstances, to the actual size of the colloid particles without the water envelope. Moreover, this effect will be further reduced because the size of the particles is greater than the wave-length of the light employed. If there is any effect of hydration on the transmitted light at all, it will be in the beginning when the particles are not large as in the later stages of coagulation. This will affect the transmitted light in the opposite sense to that in which it affects the viscosity measurements. Thus, a greater decrease in the deflection will be observed in the initial stages of coagulation and, hence, the slow coagulation should not be observed.

### Apparatus.

The light from a gas-filled Osram lamp (60 watts-30 volts) enclosed in a wooden box lined inside with asbestos and having a glass window ( $r = 2\text{ cms.}$ ) is first allowed to pass through a condenser ( $\gamma = 9\text{ cms.}$ ) to obtain a parallel beam of light. This is allowed to pass from a window ( $4 \times 6\text{ cm.}^2$ ) through 4 per cent.  $\text{Cu}(\text{NO}_3)_2$  solution contained in a rectangular optical glass cell (30 c.c. capacity). The light is thus deprived of ultraviolet rays and is rich in light waves from the violet to yellow range only. In this way any effect of light of short wave-lengths is eliminated. After passing through an optical glass colloid cell (100 c.c. capacity) the light then falls on a photo-electric cell, enclosed in a box, through a glass window ( $r = 1\text{ cm.}$ ). The  $\text{Cu}(\text{NO}_3)_2$  solution cell as well as the colloid cell are placed in a tank (12 cms. wide externally) with two glass windows ( $4 \times 6\text{ cm.}^2$  and  $2.5 \times 1.5\text{ cm.}^2$ ) for the passage of light as mentioned above. The tank is maintained at  $25^\circ\text{ C.}$  by means of a 10 per cent.  $\text{CaCl}_2$  solution thermoregulator. Thus the distance between the photo-electric cell and the source of light is 21 cms. Arrangement is made to keep the water in the tank running continuously, thus avoiding as far as possible the accumulation of dust particles which might scatter some light. The water is first passed through a glass-wool filter.

The vacuum photo-electric cell (supplied by G.E.C.) contains potassium as the sensitive material. The cell has a large window (specially designed to work with diffuse light) and contains a central plate cathode, while the silvered surface of the bulb is the anode. This type of cell is rather more sensitive than the one with a small window when exposed to diffused light; its main advantage is that it gives a more accurate proportionality between the photo-electric current and illumination. Its sensitivity is independent of temperature within atmospheric limits.

The photo-electric cell is connected to a very sensitive "Broca" galvanometer supplied with a lamp and scale. The figure of merit of the galvanometer is determined every day before each set of experiments and a suitable correction applied to the readings for any variation in the sensitivity of the galvanometer. A high tension Exide battery (Type W.J.) of 40 volts and a Mullard resistance of 180,000 ohms are also introduced in the circuits, the negative pole of the battery being connected to the cathode of the photo-electric cell. The high tension battery amplifies the photo-electric current while the large resistance serves to protect the photo-electric cell and the galvanometer in case too large a potential is accidentally applied. If the voltage varies during an experiment, a suitable

<sup>20</sup> Cf. Kraemer and Dexter, *J. physical Chem.*, 1927, 31, 779.

## THE KINETICS OF COAGULATION

correction can be applied from the photo-electric current-voltage curve for the particular photo-electric cell used.

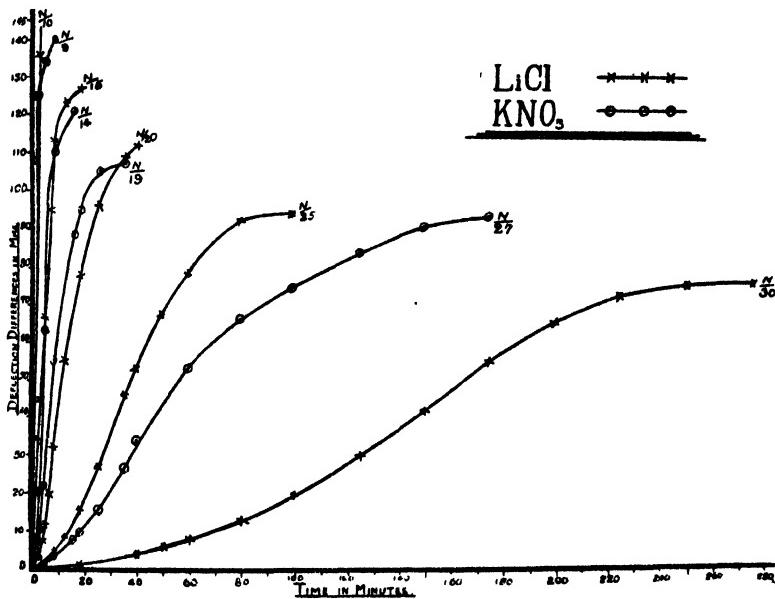


FIG. 1.

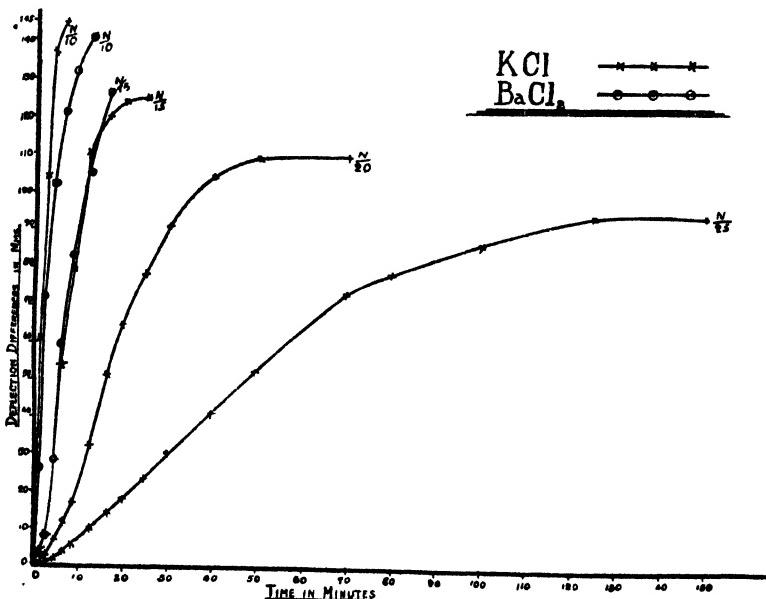


FIG. 2.

The galvanometer is so adjusted that with water alone in the colloid cell, a deflection of 335 mm. on the scale is produced. With 20 c.c. of

water and 20 c.c. of colloid, the deflection is 328 mm.; this gives the zero reading, *i.e.* the initial transparency before coagulation sets in. A blank experiment, with the colourless electrolytes employed in the investigation in the colloid cell, showed that the galvanometer reading, *viz.* 335 mm. is not at all affected by them. When taking readings 20 c.c. of the sol (at 25° C.) and 20 c.c. of the electrolyte (at 25° C.) are first mixed in a test-tube by adding the electrolyte to the sol along the wall of the test-tube and pouring the mixture back into the electrolyte-tube, the method of mixing being maintained uniform throughout. The mixture is immediately transferred to the colloid cell. The time of mixing is carefully noted. The photo-electric cell is exposed to the light at intervals of a few minutes by means of a sliding asbestos screen interposed between the source of light and the condenser. The intensity of the light at its source is checked by means of an ammeter reading to  $1/20$  of an ampere. Further the ammeter scale is read by means of a microscope with a scale inside (1 division of the ammeter = 50 divisions of microscope scale). Before each experiment, the correction to be applied for the variation of the current by 1 division of the microscope scale is determined and the readings of the galvanometer are accordingly corrected for the variation of the illumination during each set of experiments. If there is great variation during an experiment, the current is brought to the original reading by means of a sliding resistance which is introduced in the light circuit. The distances between the light source and various cells are permanently fixed.

As the size of the particles increases with the progress of coagulation, the galvanometer deflection decreases. It reaches a minimum in all cases, then (with concentrated electrolytes) it begins to increase while (with dilute electrolytes) it remains constant for a time and then begins to increase. The height of the box in which the photo-electric cell is contained is adjusted in such a way that with 40 c.c. of the mixture in the colloid cell,

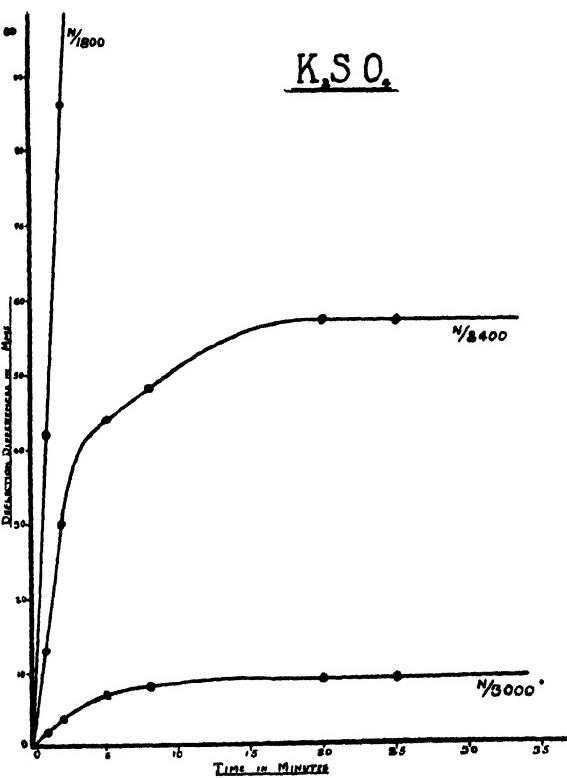


FIG. 3.

the level of the surface of the mixture in the cell forms a tangent to the top of the circular window ( $r = 1$  cm.) of the photo-electric cell box. Thus the settling of the coagulum as a whole or its separation into big flakes, when the coagulation is over, is observed immediately without any difficulty. The increase in the deflection of the galvanometer shows that sedimentation has set in.

### Preparation of the Sol.

Thorium oxide sol was investigated as it has not been much studied. Several methods of preparation are known. The condensation method of

Biltz<sup>21</sup> was not chosen as much thorium passes out during dialysis and hence a sol of any desired concentration could not be prepared. It was decided to utilise Muller's method,<sup>22</sup> by which a sol of any desired concentration can be prepared, as almost all the thorium is in colloidal condition of  $\text{ThO}_2$  from the beginning and hence no thorium passes out during dialysis.

Twenty-five g. of thorium nitrate were dissolved in about 300 c.c. of warm distilled water and the hydroxide precipitated by adding excess of ammonia. The precipitate was rapidly

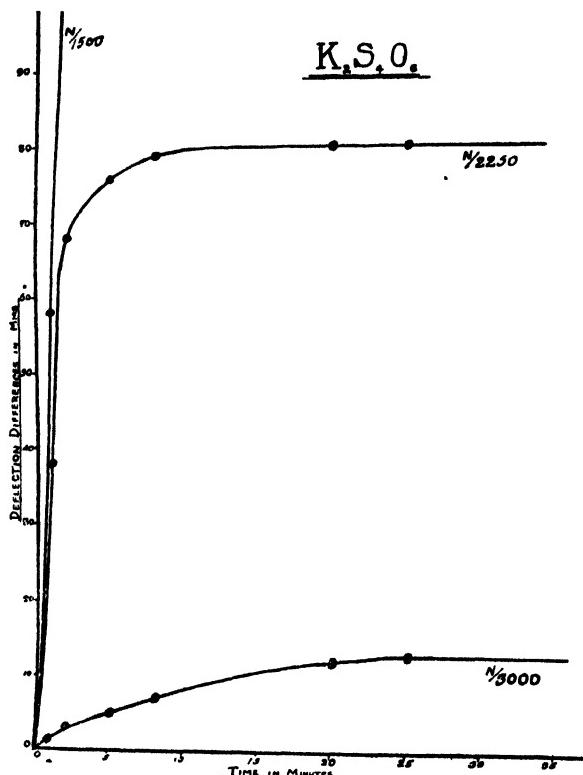


FIG. 4.

washed with hot water till free from ammonia and suspended in two litres of water. The suspension was heated nearly to the boiling-point and  $N/20$  HCl was added in quantities of 2 c.c. at intervals. The evaporated water was replaced from time to time. After adding nearly 320 c.c. of HCl and heating for nearly 7 hours, an opalescent sol was obtained. This was transferred to a parchment bag suspended from the rim of a rectangular trough. Distilled water was allowed to flow through the trough at the rate of one litre per hour while the dialysate was run out at the same rate. The sol was removed to a resistance glass flask after dialysis. During the dialysis practically no thorium passed out in the dialysate.

<sup>21</sup> Ber., 1902, 45, 4431-4438.

<sup>22</sup> Allgemeine Chemie der Kolloid, 1907.

The glass ware used in this investigation was of resistance glass and it was cleaned every time with the usual precautions. The conductivity of the

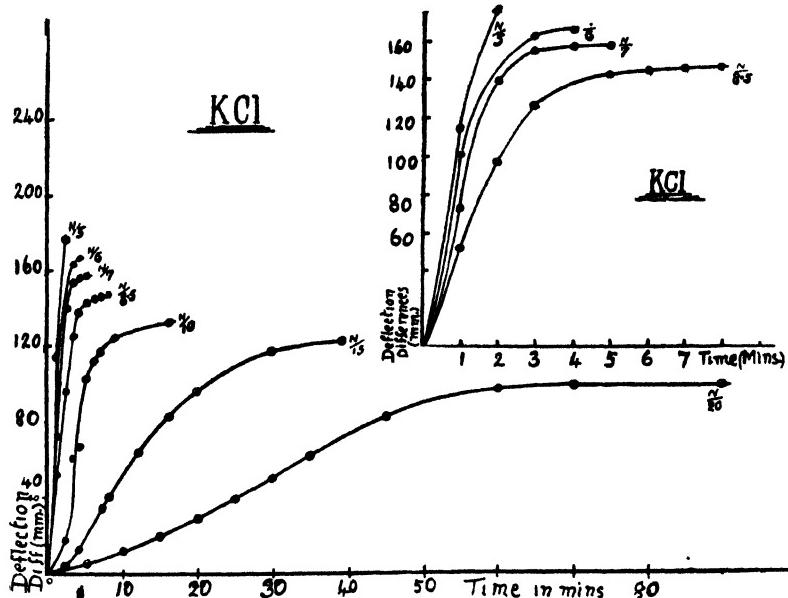


FIG. 5.

water used in making up solutions varied from  $-1.0$  to  $2.0 \times 10^{-6}$  mhos. The electrolytes were prepared from "B.D.H., A.R." salts which were further twice recrystallised from conductivity water under suitable conditions.

### Results.

The coagulation experiments were carried out as already described. A blank experiment with  $\text{ThO}_2$  sol, showed that it was not sensitive to light even when exposed for nearly two hours. Each experiment was duplicated and the results of the two experiments did not vary beyond 2 to 3 per cent. These values were plotted and an average curve for each electrolyte concentration obtained.

The curves are shown in Figs. 1 to 5. Figs. 1 to 4 apply to a sol (A) dialysed for 7 days and Fig. 5 to a sol

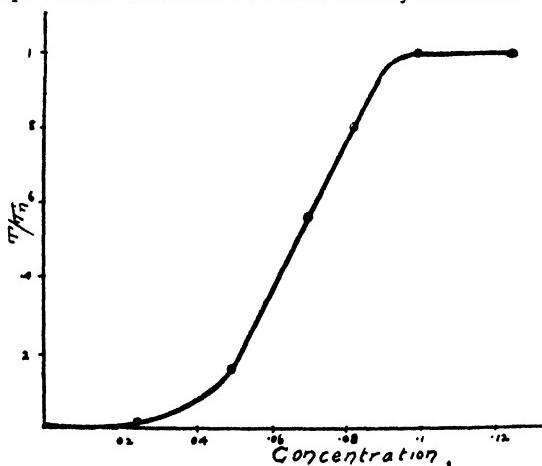


FIG. 6.

## THE KINETICS OF COAGULATION

(B) dialysed for 6 days. Sol A contained 4.95 g. and sol B, 4.90 g. ThO<sub>2</sub>/litre respectively. The concentrations given are those of the electrolytes before mixing. "Deflection difference" means the difference between the deflection (328 mms.) for unchanged sol and the deflection after the time interval indicated.

## Discussion.

According to Smoluchowski's theory of the kinetics of coagulation,<sup>1</sup> the coagulation velocity curves of a colloid with the same electrolyte of different concentrations must be related to one another. If this be the case, we should be able to pass from the coagulation velocity curve with the electrolyte of concentration C to that with concentration C<sub>1</sub> by multiplying the times T for the different stages of coalescence of the former by a constant factor. In other words, the values of the ratios T<sub>1</sub>/T, T<sub>2</sub>/T, T<sub>3</sub>/T, etc., must be the same for every electrolyte concentration (T, T<sub>1</sub>, T<sub>2</sub>, T<sub>3</sub>, etc., are the respective times for the same stage in coalescence with electrolyte of concentrations C, C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, etc.). In Tables I. and Ia. the values of this

TABLE I.—(SOL A.).

Deflection Differences in Mm.	LiCl					KNO <sub>3</sub>			
	N/10 T.	N/15 T <sub>1</sub> /T.	N/20 T <sub>2</sub> /T.	N/25 T <sub>3</sub> /T.	N/30 T <sub>4</sub> /T.	N/9 T.	N/14 T <sub>1</sub> /T.	N/19 T <sub>2</sub> /T.	N/27 T <sub>3</sub> /T.
3	I	6.3	25.0	155.00	875.0	I	13.3	33.3	233.0
8	I	5.0	25.0	100.00	500.0	I	13.3	25.3	200.0
18	I	4.2	20.2	74.10	305.4	I	11.5	19.4	154.3
28	I	4.5	17.5	60.25	300.0	I	9.5	17.8	141.2
48	I	4.6	15.7	52.14	228.6	I	7.5	15.5	120.0
68	I	4.4	15.5	52.20	210.0	I	6.3	15.2	136.0
88	I	4.3	16.8	56.50	—	I	5.5	18.6	175.7
108	I	4.4	21.2	—	—	I	7.6	—	—

TABLE Ia.—(SOL B.).

Deflection Differences in Mm.	KCl						
	N/5 T.	N/6 T <sub>1</sub> /T.	N/7 T <sub>2</sub> /T.	N/8.5 T <sub>3</sub> /T.	N/10 T <sub>4</sub> /T.	N/15 T <sub>5</sub> /T.	N/20 T <sub>6</sub> /T.
7	I	1.60	2.6	2.5	10.0	54.0	140.0
12	I	1.40	2.0	2.1	8.1	38.0	105.0
17	I	1.40	1.9	2.0	8.0	33.6	100.0
22	I	1.30	1.9	2.4	7.8	30.6	90.0
27	I	1.25	1.9	2.4	7.0	26.6	84.3
32	I	1.25	1.8	2.4	6.9	25.2	81.5
37	I	1.20	1.7	2.4	6.0	23.4	75.0
42	I	1.18	1.6	2.3	5.8	22.2	70.1
52	I	1.18	1.7	2.3	5.5	21.7	67.8
62	I	1.18	1.7	2.3	5.0	21.3	64.8
72	I	1.20	1.6	2.3	5.0	21.3	62.7
82	I	1.16	1.6	2.4	4.8	22.0	62.5
92	I	1.15	1.6	2.5	4.6	23.0	66.1
102	I	1.15	1.6	2.7	5.4	25.0	—
112	I	1.20	1.7	3.0	6.5	27.3	—
132	I	1.20	1.7	—	—	—	—

ratio for some of the electrolytes are calculated by taking the values of T for the same stage in coalescence from the respective coagulation velocity curves.

It will be seen from the tables that the value of the ratio  $T_n/T$  is nearly constant for  $N/15$  LiCl, but that for other LiCl concentrations, the values vary greatly with the advance in the stage of coalescence, the variation becoming more and more with the increase in dilution of the electrolyte. The same is the case with  $\text{KNO}_3$ . In case of KCl the values of the ratio are nearly constant for concentrations  $N/6$ ,  $N/7$ , and  $N/8.5$ . For  $N/10$ ,  $N/15$ , and  $N/20$  KCl, the values vary as in the case of LiCl and  $\text{KNO}_3$ .

The reciprocal of the value of the ratio  $T_n/T$  will be proportional to the coagulation velocity. It will be seen from Fig. 6 that the velocity is greatly reduced with increase in dilution of the coagulator; at very great dilutions the velocity will be reduced to zero. Further, at higher concentrations a limiting value is reached. This is in agreement with Freundlich's<sup>23</sup> theory of coagulation.

According to Gann<sup>10</sup> and others, the coagulation process resembles an autocatalytic reaction. He has calculated the value of the velocity constant K according to the equation,

$$\frac{dx}{dt} = K(1 + bx)(1 - x).$$

The value of b was taken from the ordinates of the point of inflection on the  $\frac{dx}{dt} - t$  curve.

In Tables II. and IIa. are given the values of the velocity constant K

TABLE II.—(SOL A.).

Electrolyte.	Conc.	b.	t (Mins.).	K		
				Max.	Min.	Mean.
LiCl*	$N/20$	0.015	9 to 30	0.0276	0.0230	0.0264
	"	0.005	35 " 80	0.00805	0.00736	0.0755
	$N/30$	0.0007	150 " 250	0.00195	0.00161	0.00184
KCl*	$N/15$	0.027	8 " 15	0.0660	0.0621	0.0639
	$N/20$	0.0116	16 " 40	0.0200	0.0184	0.0192
	$N/25$	0.005	30 " 100	0.0062	0.0051	0.00585
$\text{KNO}_3^{**}$	$N/14$	0.55	63 " 110	0.126	0.115	0.121
	$N/19$	0.033	5 " 18	0.043	0.036	0.040
	$N/27$	0.0035	40 " 125	0.0058	0.0051	0.0053
BaCl <sub>2</sub> *	$N/15$	0.02	6 " 12	0.069	0.051	0.065

TABLE IIa.—(SOL B.).

Electrolyte.	Conc.	b.	t (Mins.).	K		
				Max.	Min.	Mean.
KCl***	$N/10$	0.0515	3 to 7	0.165	0.138	0.155
	$N/15$	0.0166	12 " 30	0.0488	0.0452	0.0471
	$N/20$	0.007	15 " 45	0.0133	0.0073	0.0103

\* Maximum deflection difference for concentrated solutions = 200 mm.

\*\* " " " = 180 "

\*\*\* " " " = 180 "

## THE KINETICS OF COAGULATION

calculated according to this equation,  $x$  being put equal to - deflection difference at time  $t$ /maximum deflection. The fourth column gives the limits within which the calculation was applied.

The values of  $K$  for any one electrolyte concentration are fairly constant in many cases, which justifies the belief that the nature of the coagulation process is autocatalytic.

It will be seen that the values of the velocity constant for  $N/20$  and  $N/25$  LiCl are greater than those for  $N/20$  and  $N/25$  KCl (Table II.) respectively. This is due to the greater stabilising power of K ion as compared with Li ion. The exact manner in which this influence affects the course of coagulation as well as the conditions under which it makes itself most conspicuous will be dealt with elsewhere.

$$\text{According to Paine,}^9 \quad T_n/T = (c/c_n)^P$$

$$\text{or} \quad \log T_n - \log T = P(\log c - \log c_n).$$

In Tables III and IIIa. are calculated the values of  $P$  for different values of  $c$ .

TABLE III.—(SOL A.).

(Average values of  $T_n/T$  taken from Table II.)

Value of T for $N/10$ LiCl as Standard.			Value of T for $N/9$ $\text{KNO}_3$ as Standard.		
$T_n/T$	$C/C_n$	P.	$T_n/T$	$C/C_n$	P.
4.7	1.5	3.82	9.34	1.555	5.06
19.6	2.0	4.29	20.73	2.111	4.05
78.6	2.5	4.76	165.74	3.000	4.65
413.1	3.0	5.48	—	—	—

TABLE IIIa.—(SOL B.).

(Average values  $T_n/T$  taken from Table IIa.)

Value of T for $N/5$ KCl as Standard.			Value of T for $N/10$ KCl as Standard.		
$T_n/T$	$C/C_n$	P.	$T_n/T$	$C/C_n$	P.
1.25	1.2	1.34	0.160	0.500	2.6
1.79	1.4	1.73	0.197	0.600	3.2
2.40	1.7	1.65	0.275	0.700	3.6
6.43	2.0	2.68	0.411	0.855	5.6
27.70	3.0	3.02	3.880	1.510	3.3
82.30	4.0	3.18	11.300	2.000	3.5

Paine found the value of  $P$  for univalent coagulating ions to be between 5 and 6; Hatschek<sup>15</sup> on the other hand, found 12. From the above tables it will be seen that the value varies with the dilution and also with the concentration of the electrolyte taken as standard.

Freundlich<sup>14</sup> has derived an empirical equation connecting the velocity constant  $K$  with concentration  $C$  which has the form

$$K = \text{const } K \times C^P$$

$$\text{or } \frac{K}{K_n} = \left( \frac{C}{C_n} \right)^P$$

$$\text{or } \log K - \log K_n = P(\log C - \log C_n)$$

In the following Tables IV. and IVa. are calculated the values of P for different concentrations, the value of the velocity constant being the average taken from Tables II. and IIa.

TABLE IV.—(SOL A.).

K for $N/30$ LiCl as Standard.			K for $N/25$ LiCl as Standard.			K for $N/20$ LiCl as Standard.		
K/K <sub>n.</sub>	C/C <sub>n.</sub>	P.	K/K <sub>n.</sub>	C/C <sub>n.</sub>	P.	K/K <sub>n.</sub>	C/C <sub>n.</sub>	P.
14.340 4.103	1.5 1.2	6.4 7.7	3.496 0.2438	1.200 0.833	6.8 7.7	0.2859 0.0700	0.800 0.666	5.6 6.4

K for $N/25$ KCl as Standard.			K for $N/27$ KNO <sub>3</sub> as Standard.		
K/K <sub>n.</sub>	C/C <sub>n.</sub>	P.	K/K <sub>n.</sub>	C/C <sub>n.</sub>	P.
10.923 3.282	1.666 1.250	4.7 5.3	20.940 7.547	1.93 1.42	4.6 5.7

According to Freundlich the value of P varies from 2 to 7. It will be seen from the above tables that the variation is practically within these limits.

A possible explanation of the "S" shaped curves may be arrived at by extending Freundlich's theory of coagulation. This is based on the fact that coagulation commences though the colloid is still far from the iso-electric point and postulates that the velocity of coagulation is a function of the electrokinetic *P.D.* between the particles and the dispersion medium. If now we assume that the decrease in *P.D.* may under certain circumstances take place at a relatively slow rate we should get in those cases a gradual acceleration of the coagulation at first and hence an "S" shaped curve. The observations of Powis<sup>24</sup> on oil emulsions show that the establishment of ionic equilibrium in such disperse systems may take considerable time. On the other hand when the electrolyte is of such a nature or at such a concentration that the *P.D.* is reduced immediately to its new value the velocity of coagulation will reach its maximum value at once. This apparently happens at high concentrations of univalent ions (Figs. 1, 2, and 5), and at all concentrations of bivalent ions<sup>10</sup> (Figs. 3 and 4). The behaviour of the latter may be related to their great adsorbatibility.<sup>25</sup>

Another factor which may account, at least in part, for the change from slow to rapid coagulation when the electrolyte is sufficiently dilute is indicated in the experiments of Wiegner<sup>12</sup> and Galecki<sup>13</sup> who found from ultramicroscopic observations with gold sols that the small particles showed a greater

<sup>24</sup> *Z. physikal. Chemie.*, 1915, **89**, 179.

<sup>25</sup> Freundlich, *Kolloid Z.*, 1907, **1**, 321; Bancroft, *J. physical Chem.*, 1915, **19**, 349; Weiser, *J. physical Chem.*, 1919, **23**, 205.

tendency to coalesce with larger ones than with one another. The same thing has also been observed by the writer with gum dammer suspension. Equal volumes of  $N$  KCl and gum dammer were mixed in a test-tube and the mixture transferred to a rectangular cell. After the addition of KCl hundreds of small particles were observed in the mixture. On allowing it to stand for a time it was observed without difficulty that smaller particles settled on larger ones and after an hour only four big particles remained suspended in the liquid. These four settled without any further coalescence and the supernatant liquid did not contain any colloidal gum dammer. If this be the case we should expect acceleration of the coagulation velocity as the degree of coalescence increases.

Odén<sup>2b</sup> found that the ultimate size of the aggregates in a coagulated  $\text{BaSO}_4$  suspension depended upon the concentration of the coagulator. The same thing apparently applies to  $\text{ThO}_2$  sol, for, as will be seen from Figs. 1 to 5, the maximum deflection decreases as the electrolyte becomes more dilute. The viscosity measurements of Gann<sup>10</sup> show a similar effect. The amount of light scattered when the limiting stage of coalescence is reached is less for bivalent than for univalent coagulating ions. This may be connected with the large difference in the rates of coagulation, the coagulation process being thus comparable with crystallisation from solution as far as crystal size is concerned.

### Summary.

1. The velocity of coagulation of colloidal thorium oxide has been measured by a very accurate optical method.
2. It has been shown that the constancy of the ratio  $T_n/T$  demanded by Smoluchowski's theory is maintained only up to a certain coagulator concentration.
3. The view that the nature of the coagulation process is autocatalytic is supported by these experiments. The velocity constant  $K$  has been calculated according to the equation  $\frac{dx}{dt} = K(1 + bx)(1 - x)$ , the value of  $b$  being equal to  $\frac{dx}{dt}$  at a point of inflection of the  $x - t$  curve. A fairly constant value is obtained.
4. Reasons for the non-observance of the "slow coagulation" region by many workers have been advanced.
5. It is found that the value of  $P$  according to the equations of Paine and Freundlich varies with the dilution and depends upon the electrolyte concentration which is taken as standard.
6. The difference in the value of  $K$  for corresponding concentrations of LiCl and KCl is explained as due to the influence of the ion carrying the same charge as the colloid.
7. The theory developed by Freundlich for rapid as well as slow coagulation is supported and extended.
8. The observance of the decrease in the maximum deflection difference with the increase in dilution of the electrolyte supports the results of Odén on  $\text{BaSO}_4$  suspension, showing that the ultimate size of the particles varies with the concentration of the coagulator. The peculiar behaviour of bivalent ions is explained on the basis of their great adsorbability and the consequent initial rapid rate of coagulation.

I have great pleasure in thanking Professor Sir James Walker for his constant interest in the work and for the facilities in carrying it out. My thanks are also due to Mr. T. R. Bolam and Dr. E. B. Ludlam for some valuable suggestions.

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## PROPERTIES OF POWDERS. PART IX.

### THE SCATTERING OF LIGHT BY GRADED PARTICLES IN SUSPENSION.

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#### I. Introduction.

Previous work, both practical and theoretical, on the scattering of light has been concerned with particles whose diameter was of the order of the wave-length of the light. The theoretical aspects of this problem were considered by Lord Rayleigh.<sup>1</sup> On the practical side, Keen and Porter<sup>2</sup> and Raman<sup>3</sup> have studied the colour produced when minute particles of sulphur are precipitated from thiosulphates by the action of acids, whilst Wells<sup>4</sup> and Renwick<sup>5</sup> have recently studied the turbidity produced by precipitates of the type used in photographic emulsions. Work has also been done by Raman and others on the scattering of light by vapours, liquids and solutions. The work described in the present paper is of a different order, since it deals exclusively with particles produced by mechanical grinding, and graded by elutriation in a slow current of water. These particles, which have a diameter of about 10 to  $100\mu$  (0.01 to 0.1 mm.) are therefore intermediate in size between the very small particles of an ultramicroscopic colloidal suspension ( $d = 0.25$  to  $0.006\mu$ ) and the relatively large particles ( $>100\mu$ ) which are left behind when the "grit" is separated from a coarsely ground powder by elutriation in water. The purpose of the experiments was to find out the extent to which the opacity of a pigment may be increased by reducing the average size of the particles, and the range selected was intended to represent the ultimate products of fine-grading on a large scale, assisted perhaps by some process of grading which would return the coarser particles to the mill to be reground. The main result of the experiments is to indicate that a *maximum opacity* must exist for a given surface-concentration of the powder, but that this maximum lies well beyond the limits of fineness that can be attained by the methods of grinding now in general use. There is, therefore, a wide margin available for increasing the covering power of a given weight of material; but further investigation is required to show how far the increased covering-power may be counterbalanced by an increase in the quantity of the medium used to convert the dry powder into a paint.

<sup>1</sup> *Collected Papers*, 5, 547.

<sup>2</sup> *Ibid.*, 1921, 100, 102.

<sup>3</sup> *Phot. Journ.*, 1927, 67, 185.

<sup>4</sup> *Proc. Roy. Soc.*, 1914, 89, 370.

<sup>5</sup> *Chemical Reviews*, 1927, 3, 331.

## 2. Grading of Particles.

The material selected for the first experiments was a very good sample of ground barytes. When examined under the microscope, the particles were seen to consist of transparent cleavage-fragments of the original crystals. The powder was graded in elutriators of the type described in Part V. of the present series of papers ("A new elutriator for rapid use").<sup>6</sup> For water-velocities of 1 to 12·5 mm. per second a 3 cm. tube was used, while for speeds less than 1 mm. per second a large (2½ litre) cylindrical separating funnel was used to give a tube-diameter of about 12 cm. The rate of flow was regulated by using a number of different jets for the overflow; it was kept steady by maintaining

a constant head of water, and the velocity was determined by measuring the total flow of water per minute. The maximum velocity of flow was 12·5 mm and the minimum 0·05 mm. per second; between these limits 12 intermediate velocities were used to grade the sample into 13 fractions. Tap water was used, and no attempt was made to correct for small variations of temperature ( $\pm 1^{\circ}$  C.), since these have already been shown<sup>6</sup> to be unimportant.

It has been stated that the velocity of the water in an elutriator is a maximum on the centre line of the tube, and falls off uniformly to zero on approaching the walls; thus it has been calculated that the maximum velocity in the central line of the

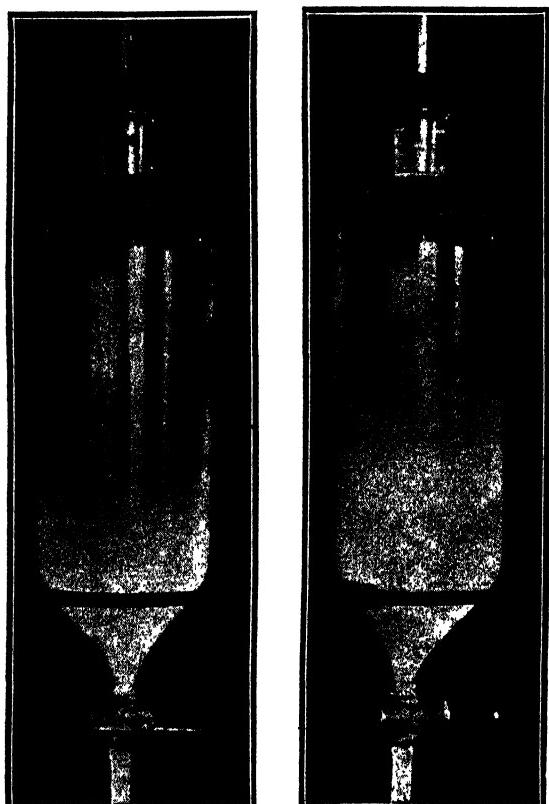


FIG. I.

lower narrow tube of Crook's elutriator is twice as great as the average velocity deduced from the overflow of the jet.<sup>7</sup> In both of the elutriators used in our own experiments, however, it was noticed that when the water-current was turned on, after the water in the elutriator had been stationary overnight, the turbid liquid was bounded by a horizontal plane (Fig. 1) which persisted throughout the length of the tube from the point where swirling ceased. This observation proved conclusively that the

<sup>6</sup> *Trans. Faraday Soc.*, 1922, 18, 32.

<sup>7</sup> Baker, *Geol. Mag.*, 1920, 57, 321; compare Boswell, *Trans. Faraday Soc.*, 1922, 18, 36.

velocity of the water was constant over the cross-section of the tube. It is suggested that this result may be due to the presence of the solid in the conical portion of the elutriator; but it was found to be independent both of the mass of solid present and of the velocity of the water.

### 3. Measurement of Particles.

In order to determine the average size of the particles in the various fractions, the "diameter" of 100 particles of each grade was measured by means of a microscope with a calibrated eye-piece scale. As far as could be judged, the particles of each fraction were of approximately uniform bulk, but owing to their irregular shape there was a considerable variation in the readings of the "diameter." When, however, the readings were grouped in 4 sets of 25, the difference between the largest and smallest average was always less than 5 per cent. The square of the average "diameter" of 13 fractions of barytes is set out in Table I.

TABLE I.—ELUTRIATION OF BARYTES.

Elutriator.	Limits of Water-velocity. (Mm. Per Sec.).	Water-velocity (Mean). (Mm. Per Sec.).	Mean "Diameter" of Particles. ( $10^{-4}$ Cms.)	Square of Diameter. $10^{-8}$ Sq. Cms.
Large.	0·050 to 0·075	0·0625	7·09	50·3
	·075 to ·100	0·0875	9·07	82·3
	·10 to ·20	0·150	14·2	202
	·20 to ·30	0·250	16·8	276
	·50 to ·75	0·625	24·7	610
	·75 to 1·00	0·875	28·3	810
Small.	1·0 to 2·0	1·50	41·5	1722
	2·0 to 3·0	2·50	57·4	3295
	3·0 to 4·0	3·50	66·5	4422
	4·0 to 5·0	4·50	74·5	5550
	5·0 to 7·5	6·25	90·2	8136
	7·5 to 10·0	8·75	108·6	11,790
	10·0 to 12·5	11·25	126·7	16,050

Lowry and McHatton<sup>6</sup> found that the mean diameter of particles of barytes was related to the water velocity in the elutriator according to the formula :

$$\log d = \bar{z} \cdot 67 + kv$$

where  $d$  is the mean diameter

$v$  is the water velocity

$k$  is a constant depending on diameter of the tube and temperature of the water.

This formula could be used to express the data of Table I., over the range within which it was first applied, namely from 4 to 8 mm. per second; but it broke down completely for smaller velocities. Fig. 2 (a) and (b), in which the water-velocities in the large and small elutriator respectively are plotted against the *square* of the mean diameter, indicates that there is a rough proportionality between these quantities, as required by Stokes' Law, since the points all fall fairly near to lines through the origin. A closer agreement can be obtained in the case of the small elutriator by ignoring the origin,

and drawing the line through a point rather below the axis of zero diameter, i.e., by supposing that Stokes' Law applies when a constant increment is

a. Large Elutriator.

b. Small Elutriator.

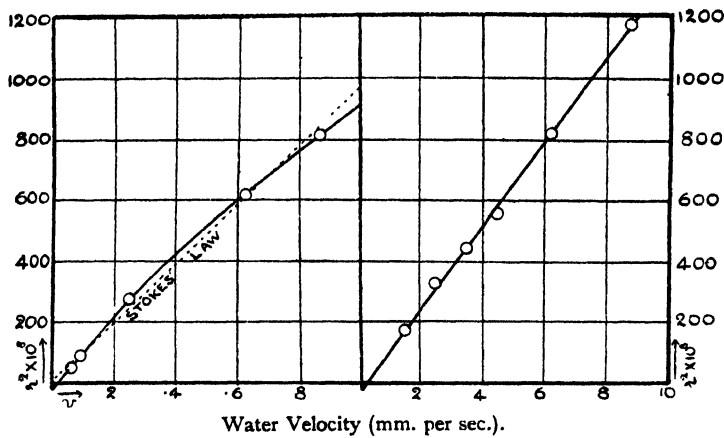


FIG. 2.—Elutriation of Barytes.

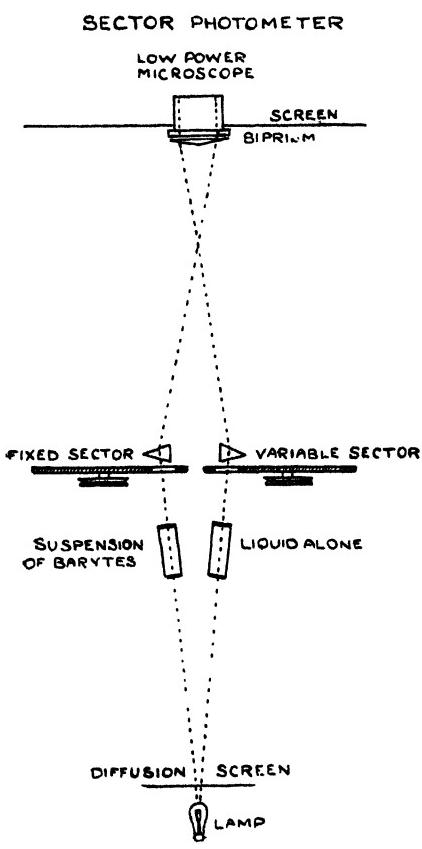


FIG. 3.

added to the square of the diameter, or by supposing that the irregular particles behave like spheres whose diameter is slightly larger than their own mean diameter. The data for the large elutriator lie on a curve which approximates to a straight line passing through the origin although the curve cuts the axis of diameter squared in a negative value as in the case of the large elutriator. The slope of the straight line is 1380 for the small elutriator and 980 for the large one. We therefore conclude that:—

(1) With a tube 3 cm. in diameter and velocities from 1 mm. to 12.5 mm. per second, Stokes' Law is obeyed within the limits of accuracy of the experiment, assuming the particles to behave as spheres of slightly larger diameter than the mean width of the particles.

(2) With a tube 12 cm. in diameter, and velocities below 1 mm. per second, Stokes' Law is only approximately obeyed.

(3) The diameter of the tube has an effect on the constant in Stokes' formula.

#### 4. Measurement of Fraction of Light Scattered.

A Hilger sector-photometer was used to compare the intensity of two beams of light. The light passing through the "fixed" sector was reduced in intensity by passing through a suspension of barytes in a suitable liquid; a similar cell containing the liquid was placed in series with the "variable" sector in order to compensate for the loss of light in the clear medium. The instrument was arranged (Fig. 3) with the sectors in a horizontal plane, so that the light passed vertically through the suspension; and it was run at a high speed, in order to eliminate flicker, and so to make it possible to take visual observations.

Some difficulty was experienced in obtaining a uniform surface-concentration of the powder in the cell. At first, attempts were made to prepare a suspension in the form of a jelly; but later it was found better to suspend the powder in medicinal paraffin, to a known "concentration" in milligrams per c.c., and to pour the well-stirred suspension into a cell of known depth. In this way a very uniform surface-concentration in milligrams per square centimetre was obtained; and experience showed that settlement of the solid in the cell did not cause any appreciable alteration in the intensity of the transmitted light.

In order to determine the law of absorption for various surface-concentrations, experiments were made in which the fraction of light transmitted was measured for four different surface concentrations of one particular grade of powder. The results are shown in Table II.

TABLE II.—SURFACE-CONCENTRATION AND OPTICAL DENSITY OF GROUND BARYTES.

Surface-Concentration (Grams per Sq. Cm.).	Optical Density $\log \frac{I_0}{I}$ .	Ratio.
3.10	0.22	0.071
7.28	0.51	0.070
9.12	0.64	0.070
15.10	1.04	0.069

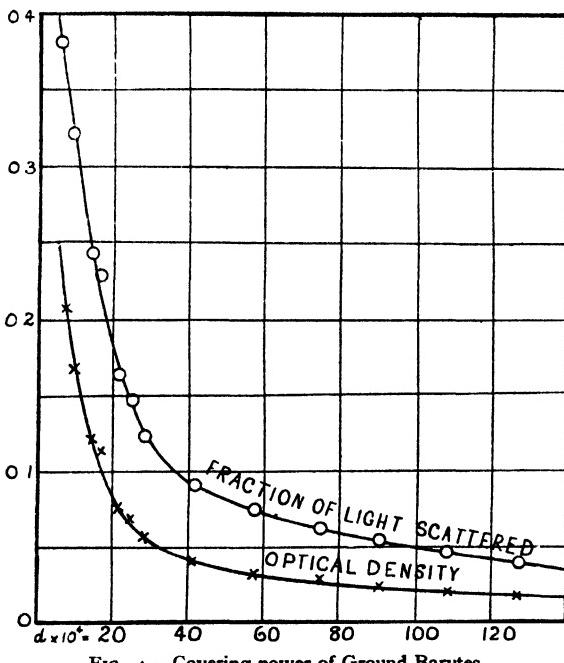


FIG. 4.—Covering-power of Ground Barytes.

When plotted against one another these numbers gave a straight line passing through the origin, showing that the optical density is directly proportional to the surface-concentration. This fact greatly simplified the succeeding work, since, instead of using the same surface-concentration for all grades of powder, the absorption for a standard surface-concentration could be deduced from observations at any convenient concentration; in particular, the surface-concentration could be adjusted so that the optical-density of the layer was of a suitable order of magnitude for accurate measurement.

The optical densities of 13 different grades of ground barytes are set out in Table III., and are plotted in Fig. 4, for a surface-concentration of 1 mg. per sq. cm.; the proportion of light  $(I_0 - I)/I$  scattered by a layer of powder of this surface-concentration is also shown for each sample.

TABLE III.—OPTICAL DENSITY OF GROUND BARYTES.

Refractive index of medium = 1.484 (by Refractometer).  
Refractive index of particles = 1.636 (Landolt and Bornstein).

Grade of Particles (Water Velocity).	Mean Diameter of Particles.	Surface- Concentration of Particles.	Optical Density $\log_{10} \frac{I_0}{I}$ .	Ratio of Optical Density to Surface Concentration.	Fraction of Light Scattered $\frac{I_0 - I}{I_0}$ .
Mm. per Sec.	$\mu$ .	Mgm. per Sq. Cm.			Reduced to 1 Mgm. per Sq. Cm.
.05 to .075	7.1	3.28	0.68	0.207	0.381
.075 to .10	9.1	4.30	0.72	0.167	0.321
.10 to .20	14.2	4.46	0.54	0.121	0.243
.20 to .30	16.8	7.96	0.90	0.113	0.229
.40 to .50	21.2	9.26	0.71	0.177	0.163
.50 to .75	24.7	10.0	0.69	0.069	0.147
.75 to 1.0	28.3	16.2	0.91	0.056	0.122
1.0 to 2.0	47.5	11.8	0.49	0.041	0.091
2.0 to 3.0	57.4	16.9	0.58	0.034	0.076
4.0 to 5.0	74.5	21.6	0.64	0.030	0.064
5.0 to 7.5	90.2	32.4	0.81	0.025	0.056
7.5 to 10.0	108.6	31.8	0.68	0.0214	0.048
10.0 to 12.5	127.6	41.7	0.73	0.0175	0.040

### 5. Covering-power of Pigments.

The curve showing the relation between light stopped and size of particles is roughly hyperbolic in form, so that most of the points are not far removed from two intersecting straight lines of very different gradient. The optical density of the powder is therefore increased only slowly by further grinding so long as the average diameter of the particles exceeds  $50\mu$  or  $\frac{1}{20}$  mm. When, however, the diameter is reduced below  $30\mu$  or  $\frac{3}{5}$  mm., corresponding with a water-velocity of about 1 mm. per second in the elutriator, the optical density of the powder increases very rapidly as the diameter of the particles is decreased. Indeed the optical density of these fine particles is so great that it might be of real service, when valuing commercial samples, to estimate them separately by elutriation at 1 mm. per second, in addition to estimating the "grit" by elutriation at 7 or 4 mm. per second.

Since barium sulphate forms transparent crystals, and would probably

be just as transparent as (say) magnesium sulphate if it could be obtained in solution, it is clear that the high covering-power of the fine particles must disappear again on further sub-division, and must therefore reach a maximum at some intermediate stage, perhaps in the range of colloidal solutions. This maximum is not reached, however, in the range of sizes that can be reached either by careful grinding, or by elutriation. Since, however, the scattering of light is a function of the refractive indices of the particles and of the medium, the present pioneer series of observations ought obviously to be followed up by measurements with particles of other substances which can be used either as pigments or as fillers, and in media such as are used to convert these substances into paints.

### 6. Summary.

- (a) A sample of ground barytes was separated into 13 fractions by elutriation at water-velocities of 0·5 to 12·5 mm. per second.
- (b) The diameters of the particles were measured and used to test the validity of Stokes' Law, as applied to crystalline particles of barytes.
- (c) The various fractions were suspended in medicinal paraffin and the light-transmission was measured. The optical density is proportional to the surface-concentration of the powder, but increases slowly as the diameter is reduced to  $50\mu$  and much more rapidly when the diameter is reduced below  $30\mu$ .
- (d) The probable existence of a maximum degree of opacity on further subdivision is indicated.

## EQUILIBRIA AT HIGH TEMPERATURES IN THE SYSTEM IRON—OXYGEN—CARBON.

BY RICHARD R. GARRAN.

(Communicated by PROFESSOR E. C. WILLIAMS.)

*Received 20th October, 1927.*

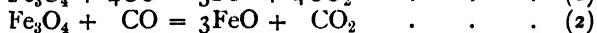
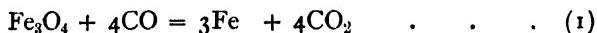
In the course of other work, need was found for accurate data concerning the equilibria set up during the reduction of oxides of iron by carbon monoxide at temperatures above  $1000^{\circ}$  C. Although there are many publications dealing with these equilibria, they are based mainly upon determinations carried out below  $1000^{\circ}$  C. or upon calculations from allied systems. A study of the literature showed that experimental data in the higher temperature region were few and these not in good agreement. Extrapolation in this region was therefore very uncertain, and it was decided to study the whole system experimentally, particularly at high temperatures, with a view to obtaining more reliable information.

The earliest work on the subject was described by Sir I. Lowthian Bell,

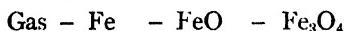
in "The Chemical Phenomena of Iron Smelting" (1872). More recent work has been summarised by Eastman,<sup>1</sup> Tigerschioëld,<sup>2</sup> and McCance.<sup>3</sup>

The system is one of three components—iron, oxygen, and carbon. Neglecting, for the present, the formation of carbides and of solid solutions, the following five phases may exist: metallic iron, ferrous oxide ( $\text{FeO}$ ), magnetic oxide of iron ( $\text{Fe}_3\text{O}_4$ ), solid carbon, and the gaseous phase, consisting of carbon monoxide and carbon dioxide. Ferric oxide ( $\text{Fe}_2\text{O}_3$ ) does not take part in the reactions here considered.

Of the three reduction reactions which may take place,



none is accompanied by any change in the total volume of the system. The equilibria set up will therefore be unaffected by changes in the gaseous pressure: and, if this pressure be arbitrarily fixed at 1 atmosphere, there are three possible pseudo-invariant systems in which one gaseous and three solid phases co-exist, namely:



If the equilibrium curves for the three reactions above-mentioned are plotted, together with that for



at 1 atmosphere total pressure, curves (1), (2), and (3) meet in a point at 50 per cent. CO and 580° C. (approximately), while curve (4) falls transversely across curves (2) and (3), as in Fig. 1. The points of intersection of these curves represent the three pseudo-invariant systems.

To the right of curve (4), i.e., at temperatures above 700° C., free carbon cannot exist as a separate phase, and there are two pseudo-bi-varient systems,  $\text{FeO} - \text{Fe}_3\text{O}_4 - \text{gas}$  and  $\text{Fe} - \text{FeO} - \text{gas}$ , the equilibria in which are dealt with in this paper. The more complex systems in which solid carbon is present, though of great importance in the theory of the blast-furnace, are not considered here. As the temperature is lowered, the deposition of carbon becomes theoretically possible on passing to the left of curve (4), i.e. at 710° C. in the case of the  $\text{Fe} - \text{FeO}$  system and at 650° C. in the case of the  $\text{FeO} - \text{Fe}_3\text{O}_4$  system. That carbon is not actually deposited in all cases is indicated by the fact that some experimental points in this region lie on curves (2) and (3) continued to the left of curve (4), while others diverge widely from these curves, and some even tend to follow curve (4). Any experimental values lying to the left of curve (4) must represent metastable equilibria, and are therefore unreliable.

Both Eastman and McCance, taking the mean of experimental values obtained by several different workers, found that the equilibrium relations in the systems  $\text{FeO} - \text{Fe}_3\text{O}_4 - \text{gas}$  and  $\text{Fe} - \text{FeO} - \text{gas}$  could be expressed in the simpler form of the Reaction Isochore, namely

$$\ln K = \frac{-Q}{RT} + C \text{ where } K = \frac{[\text{CO}_2]}{[\text{CO}]}.$$

<sup>1</sup> *J. Amer. Chem. Soc.*, 1922, 44, 975.

<sup>2</sup> *J. Kontorets Annaler*, 1923, 107, 67.

<sup>3</sup> *T. Far. Soc.*, 1925, 21, 176.

The following numerical values were given:

Observer.	System FeO - $\text{Fe}_3\text{O}_4$ - Gas. Log K <sub>2</sub> .	System Fe - FeO - Gas. Log K <sub>3</sub> .
Eastman	$-\frac{1645}{T} + 1.935$	$\frac{949}{T} - 1.140$
McCance	$-\frac{1304}{T} + 1.68$	$\frac{675}{T} - 0.87$
Calculated (see below)	$-\frac{1434}{T} + 1.723$	$\frac{868}{T} - 1.055$

Tigerschöeld gives a mean value expressed in the more complete form of the Reaction Isochore.

The disagreement between these sets of values shows how uncertain was the state of knowledge about the equilibria in question.

Hofmann<sup>4</sup> gives a method for calculating the equilibria in the system Fe - O - H from the equilibria in the analogous system Fe - O - C, and conversely, using experimental values of the equilibrium constants for the homogeneous dissociation-equilibria of water-vapour and of carbon dioxide.

The system Fe - O - H is well suited to accurate study. The expressions given in the above table were calculated, according to Hofmann's method, from the mean of the experimental values for this system given by Schreiner and Grimnes,<sup>5</sup> Wohler and Gunther,<sup>6</sup> and Eastman and Evans<sup>7</sup> over the temperature range 500°-1100° C.

The author has studied experimentally the equilibria in the system Fe - FeO - gas over the temperature range 646°-1290° C. and in the system FeO -  $\text{Fe}_3\text{O}_4$  - gas over the range 620°-1216° C.

The apparatus used consisted of a porcelain tube, 50 cm. long, 5 cm. internal diameter, heated in an electric furnace. The ends of the tube were cooled by means of annular water-jackets, and were closed by rubber bungs, one of which carried the porcelain sheath protecting the thermocouple, while the other carried a capillary tube leading to a manometer and a gas-pipette with mercury reservoir, and, through two drying-tubes containing respectively phosphorus pentoxide and calcium chloride, to a vacuum pump and to supplies of carbon monoxide and carbon dioxide. All joints in the gas-manipulation train were fused, and all taps were mercury-sealed and of capillary bore. The solid was placed in a boat in the centre of the tube. The boat was of porcelain for lower temperatures, but above 1100° C. it was found necessary to use an alundum boat, protected with a layer of crystalline alumina.

The thermocouple used was of platinum and platin-rhodium, and its E.M.F. was measured potentiometrically. It was compared at intervals during the progress of the work with a similar couple calibrated by the N.P.L.

The zone of constant temperature within the heated tube was found to be 10 cm. in length, while the largest boat used was only 6 cm. long.

The gases used were prepared as follows: carbon monoxide from pure

<sup>4</sup> Z. Elektrochem., 1925, 31, 173.  
<sup>5</sup> Z. Elektrochem., 1923, 29, 276.

<sup>6</sup> Z. anorg. Chem., 1920, 110, 311.  
<sup>7</sup> J. Amer. Chem. Soc., 1924, 46, 888.

sodium formate and sulphuric acid, washed with caustic potash, and stored over 50 per cent. sulphuric acid: carbon dioxide, from calcium carbonate and pure hydrochloric acid, washed with saturated solution of sodium bicarbonate.

The solid phases were made up from samples of "pure ferrum redactum" and "pure magnetic oxide of iron," both of which contained appreciable quantities of siliceous matter, as is shown by the following analyses:—

	Ferrum Redactum.	Magnetic Oxide.
Fe	86·7 per cent.	—
$\text{Fe}_3\text{O}_4$	10·5 "	51·5 per cent.
$\text{Fe}_2\text{O}_3$	—	32·7 "
Insoluble	2·6 per cent.	8·2 "
Water	0·2 "	7·6 "

The solid phase was made up of these two substances in such proportions that, when equilibrium had been attained, the solid phase would have the desired composition—intermediate between Fe and  $\text{FeO}$ , or between  $\text{FeO}$  and  $\text{Fe}_3\text{O}_4$ . ( $\text{Fe}_2\text{O}_3$  under the conditions of experiment is reduced

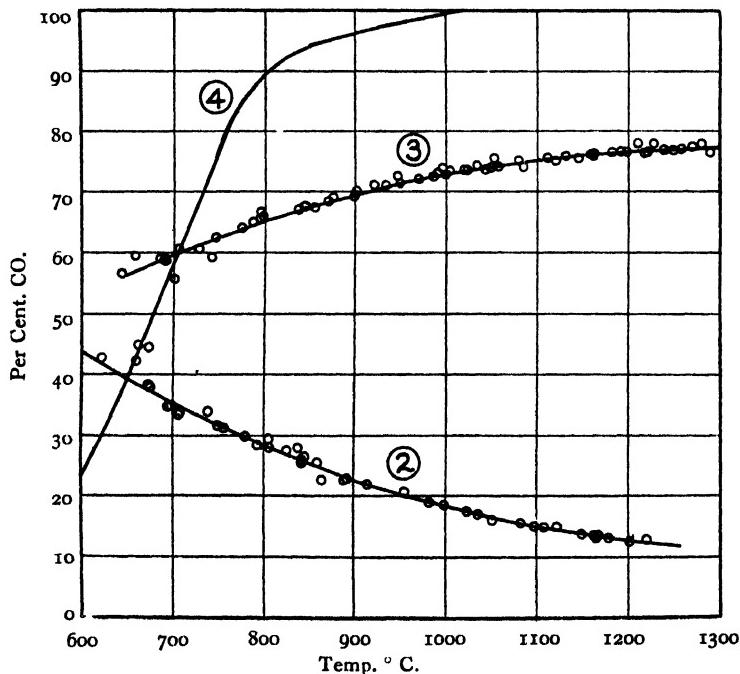


FIG. 1.

immediately to  $\text{Fe}_3\text{O}_4$  or to  $\text{FeO}$ .) To prevent, as far as possible, the two solids sintering together, they were not mixed, but placed in separate heaps. The boat was placed in the tube, which was then evacuated and heated to the required temperature, any moisture given off being absorbed in the drying-tubes. The tube was again evacuated, and CO or  $\text{CO}_2$  was then

slowly admitted to a total pressure of about 1·3 atmospheres. The temperature in the heated tube was maintained constant (by hand regulation) to within 5° C. for sufficient time for equilibrium to be established: this varied from 14 hours at 650° to 3½ hours at 1280° C. The mean of several temperature readings during the last hour of each experiment was taken: then a sample of the gas was drawn into the pipette, and subsequently analysed in a Bone and Wheeler apparatus.

The results obtained are shown in Figure 1, in which the composition of the gaseous phase is plotted against the temperature. The experimental points fall very evenly on two smooth curves, and the interpolated gas-compositions for temperature intervals of 50° C. are given in Table I.

TABLE I.

Temp. °C.	System Fe - FeO.		System FeO - Fe <sub>3</sub> O <sub>4</sub> .	
	Per Cent. CO.	Per Cent. CO <sub>2</sub> .	Per Cent. CO.	Per Cent. CO <sub>2</sub> .
600	—	—	43·7	56·3
650	56·2	43·8	39·3	60·7
700	59·5	40·5	35·3	64·7
750	62·3	37·7	31·5	68·5
800	65·0	35·0	28·2	71·8
850	67·3	32·7	25·1	74·9
900	69·3	30·7	22·4	77·6
950	71·2	28·8	20·1	79·9
1000	72·7	27·3	18·1	81·9
1050	73·9	26·1	16·3	83·7
1100	75·0	25·0	14·8	85·2
1150	75·9	24·1	13·6	86·4
1200	76·5	23·5	12·5	87·5
1250	76·9	23·1	11·7	88·3
1300	77·1	22·9	—	—

In Figure 2 the author's experimental curves are compared with those given by Chaudron<sup>8</sup> and by Matsubara<sup>9</sup> also with the curve calculated as above. It will be seen that the curves differ considerably: but the author's curve is based on a very large number of experimental results, and even those points which diverge most from the author's mean curve lie closer to it than to any other.

The experimental methods employed by the two workers mentioned above differ considerably from that used by the author. Chaudron used a dynamic method, circulating the gases continuously over the heated solid phase, and measuring the gas-composition by means of a refractometer. Matsubara, using a static method, reduced ferric oxide by successive small steps at constant temperature, and obtained his equilibrium values from a graph of gas-composition against oxygen content of the solid phase. The gas-composition remained constant when the mean composition of the solid lay between Fe and FeO, or between FeO and Fe<sub>3</sub>O<sub>4</sub>. The author's method is also static, but the required equilibrium is attained directly, and the duration of each experiment is made as short as possible.

On attempting to express these results in the form of the Reaction Isochore, it was found, on plotting log K against 1/T, that the points

<sup>8</sup> Compt. Rend., 1921, 172, 152.<sup>9</sup> Z. anorg. Chem., 1922, 124, 39.

fell on two lines definitely curved, which could be represented by the equations

$$\log K_2 = -\frac{3440}{T} - 7.91 \log T + 0.00161T + 25.860 \quad . \quad (5)$$

$$\log K_3 = \frac{4160}{T} + 9.51 \log T - 0.00121T - 31.680 \quad . \quad (6)$$

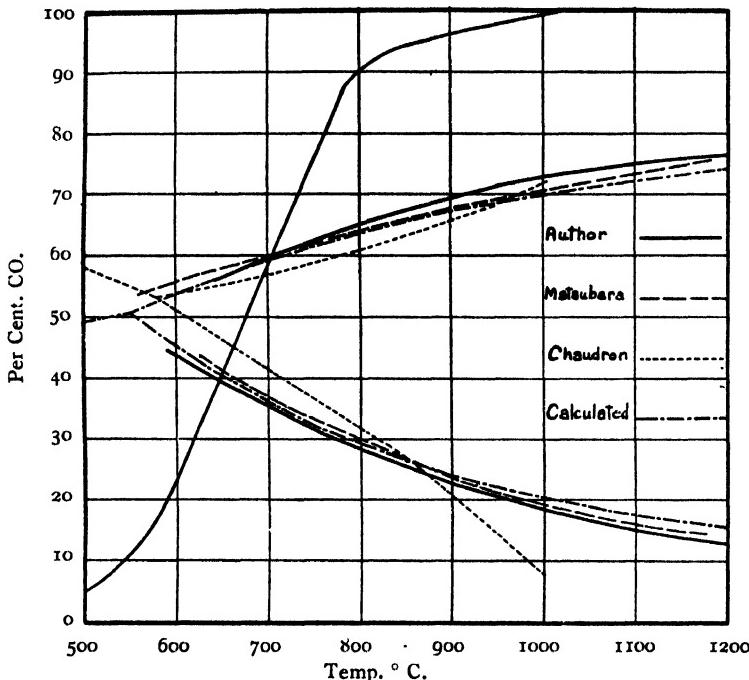


FIG. 2.

Hence, calculation of the equilibrium constants according to Hofmann's method cannot give results which are other than an approximation to the true values.

Table II. gives a comparison of the values of  $K_3$  (in the system Fe — FeO — gas) from the author's experimental values, from Equation (6)

TABLE II.—VALUES OF  $K_3$  IN THE SYSTEM Fe — FeO — Gas.

Temp. °C.	Author. Experimental.	Author. Calculated from Equation 6.	Calculated from System, Fe — O — H.	Eastman.	Tigerschloëld.	McCance.
600	—	0.984	0.869	0.883	0.793	0.800
700	0.681	0.690	0.687	0.685	0.668	0.667
800	0.542	0.516	0.568	0.555	0.569	0.574
900	0.443	0.435	0.484	0.467	0.490	0.507
1000	0.376	0.386	0.424	0.404	0.421	0.457
1100	0.333	0.337	0.378	0.356	0.364	0.419
1200	0.307	0.310	0.342	0.319	0.315	0.387
1300	0.297	0.290	0.314	0.290	0.274	0.362

above, calculated as above from equilibria in the system Fe - O - H, and according to the mean values given by Eastman, Tigerschioëld (from Matsubara's experimental results) and McCance.

Since the completion of this work, Bone, Reeve, and Saunders<sup>10</sup> have published the results of research on the reduction of ores of iron by carbon monoxide at temperatures below 700° C. The equilibria set up must be metastable: and it is interesting to note that different "resultant equilibrium ratios" (as termed by these workers) are obtained with different ores under the same conditions, suggesting that the physical nature of the ore is a factor which may influence such equilibria.

The results obtained by these authors, which deal mainly with the conditions under which deposition of carbon (according to Reaction (4)) takes place, may be readily explained by means of the curves in Figure 2. Though the existence of free carbon is possible throughout, in no case was it deposited in appreciable quantities on the reduced ore until reduction had progressed so far that all the higher oxides had been reduced to Fe<sub>3</sub>O<sub>4</sub> (550° and under) or to FeO (600° and over), and a small portion of either oxide to metallic iron, which then catalysed the reaction,



Furthermore, the higher the temperature, the less was the tendency towards carbon deposition. The experimental results are thus in good agreement at the boundary between the regions covered by this paper and by that of Bone and his co-workers.

### Summary.

Data in the literature dealing with equilibria at high temperatures in the system iron—oxygen—carbon are scarce and not concordant.

The system has been examined by calculation and by experiment: the former method has been shown to be unreliable.

Experimental results are given in the temperature range 600°-1300° C.

The author is indebted to Professor E. C. Williams for suggesting this work and for advice during its execution: to Professor C. H. Desch for his advice: and to the Committee of the Royal Society for a grant towards the expenses of the work.

<sup>10</sup> "Engineering," 1927, CXXIII, 564.

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### REVIEWS OF BOOKS.

**Sound. A Physical Text-book.** By E. G. RICHARDSON. (1927: Edward, Arnold. 15s. net.)

Whether they be sons of Jubal or of Pythagoras, worshippers at the shrine of one of the most ancient of the sciences will give a hearty welcome to the volume which has just come from the pen of Dr. Richardson.

Progress in Acoustics has for centuries been steady if unspectacular; even so it has had its ups and downs, and that spate of discoveries which, beginning near

the close of the nineteenth century, shook Victorian science out of its mood of complacency and incidentally threw the main body of Physics into the melting pot, left Acoustics more or less in the position of a Cinderella.

But various problems (some of them engendered by war conditions) pressed for solution, and a large number of these problems are definitely connected with acoustic phenomena. Sound ranging and signalling, the acoustics of auditoriums, the acoustic properties of materials, the problem of silencing—this last, one which is becoming increasingly acute in modern life—these, *inter alia*, are treated by Dr. Richardson with a fullness of reference to the original sources which enables the student easily to carry his reading to the confines of the existing knowledge on the subject.

Notable advances have also been made in certain of the purely scientific parts of Acoustics, and to some of these advances Dr. Richardson has contributed his share. Indeed, one of the most remarkable features of present-day work is the discovery of novel aspects of what were until now considered commonplace or completely investigated phenomena. Kundt's tube has by no means yielded up all its secrets; and Æolian tones and vortex formation, heat maintained sounds, edgetones, acoustic filters (giving interesting analogues to the ordinary alternating current electrical equations), and the recent advances, theoretical and practical, in subjective sound or auditions provide ample scope, of which he has fully availed himself, for the exercise of Dr. Richardson's descriptive and critical faculties. Even as we write there appears a paper from America, giving details of remarkable experimental results in the subject of "super-sonics."

The more orthodox subjects of the vibrations of strings, rods and plates, and the experimental methods for the measurement of frequency amplitude and velocity are well treated, the information being, in general, thoroughly up-to-date and the references exhaustive.

*Aliquando bonus Homerus dormitat*, and Dr. Richardson on his first page insists on talking of "elasticity," where he obviously means "inertia"; a few flag labels would considerably elucidate his diagram of the larynx for readers who are physiologists neither by aptitude nor by calling; and for reasons best known to himself he sedulously avoids the ordinary notation for partial differential coefficients.

These are, however, minor matters, and the student who has thoroughly assimilated Lamb's Dynamical Theory of Sound and Dr. Richardson's volume, which in its emphasis on experimental detail is in some measure complementary to Lamb, will be ready to study profitably the classic work of Rayleigh and of Helmholtz, even perchance to make some contribution of his own to the advancement of the science of Acoustics.

The sense of style and scholarship which pervades the book is not its least pleasing feature.

A. F.

# THE LEAD-TIN SYSTEM OF ALLOYS RE-EXAMINED BY AN ELECTRICAL RESISTANCE METHOD.

By F. H. JEFFERY.

*Received 20th December, 1927, and read before the Society,  
25th January, 1928.*

This system was investigated by Rosenhain and Tucker<sup>1</sup> by means of micrographic and thermal analysis: they did not find the upper boundary of the solid solution of tin in lead nor the tin end of the line of eutectic points, they found a line of points at 149° C. from 18 per cent. tin in lead to 62·9 per cent. but were unable to find its continuation for alloys richer in tin. Paravano and Scortecci<sup>2</sup> examined the lower boundary of the solid solution of tin in lead by measuring the electrical resistances of rods of the alloys. They did not find a line of points at 149°. Konno<sup>3</sup> also used an electrical resistance method, his method being to express the specific resistance of an alloy as a function of the temperature—the alloy was enclosed in silica tubes dipping into a larger mass of alloy contained in a crucible. His diagram did not give any indication of solid solutions of lead in tin.

## Apparatus and Procedure.

A continuous method of recording change of electrical resistance as a function of the temperature by means of two Callendar recorders was used; it has been described in a previous paper.<sup>4</sup> The alloys were made from Johnson and Matthey's best tin and assay lead foil, the mass of each being about 400 grams. Both heating curves and cooling curves were made for finding the boundaries of the solid solutions and to investigate the existence of a line of points at 149° for alloys in true equilibrium. The rates of heating and cooling were so adjusted that in nearly all cases they gave identical results. Special precautions had to be taken for alloys of composition 20 per cent. to 66 per cent. tin in lead; when cooling from liquidus to a little above the eutectic temperature the average time taken was seventy hours, and when the alloys had reached 170° C. after passing through the eutectic temperature they were held at this for about forty hours. The average rate of cooling and heating through the boundaries of the solid solutions and through the 149° line was 0·2° C. per min., but often 0·1° C. per min. was used. The rate of cooling through the liquidus was 0·2° C. per min.

<sup>1</sup> *Phil. Trans.*, 1908, **209**, 89.

<sup>2</sup> *Gazzetta Chimica Italiana*, 1920, **50**, 83.

<sup>3</sup> "Reports of the Tohoku Imperial University," 1921, **10**, 55.

<sup>4</sup> Jeffery, *Trans. Faraday Soc.*, 1927, **23**, 563.

The results are shown in the table and diagram which follow:—

Percentage of Tin.	Liquidus.	Solidus.	Boundaries below Solidus.	The Line at 149°.
0	328	—	—	—
5	314	268	120	—
7	—	252	130	—
10	301	226	151	—
13	—	206	170	—
15	—	193	179	—
20	277	183	—	no point
30	253	183	—	" "
40	234	183	—	" "
50	215	183	—	" "
60	196	183	—	" "
62·9	190	183	—	" —
65	185	183	—	—
70	191	183	—	no point
80	202	183	—	" "
90	211	183	—	" "
97	—	183	153	—
98	—	197	136	—
99	—	218	105	—
100	232	—	—	—

### Discussion of Results.

The equilibrium diagram is of the Roozeboom type 5. The *line of eutectic points* is at 183° C., the phases at the eutectic point being of compositions 16·5 per cent. tin and 97 per cent. tin. The composition of the *eutectic alloy* is 66·0 per cent. tin; Rosenhain and Tucker gave 62·9 per cent. tin. An alloy of this composition was found to have a well-defined point on the liquidus at 190° both for cooling and heating curves—the

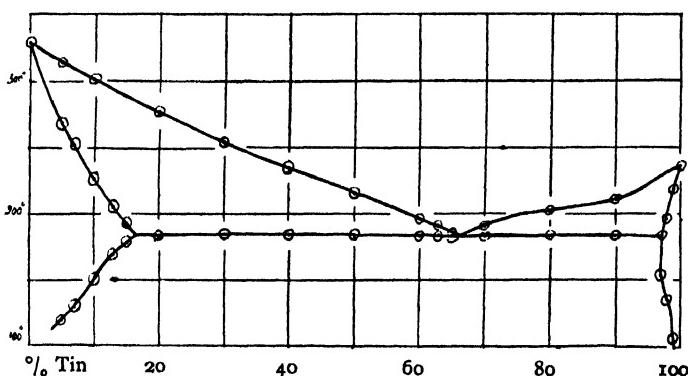


FIG. 1.—13 per cent. tin,  $\times$  370, chilled at 150° C. after 9 days at 150° C.

latter were made at the rate of 0·1° C. per min. The *line of points at 149° C.* does not appear to exist when precautions are taken to avoid metastable conditions. These arise at temperatures between those of the liquidus and the eutectic for alloys of compositions 20 per cent. to 66 per cent. tin. Alloys of composition 20 per cent. tin, 30 per cent., 50 per cent., and 60 per cent. were cooled to 170° C. without the precaution of the very slow cooling between the liquidus and temperatures just above 183° C., they were then held at 170° for about twenty to forty hours and

then cooled at  $0.2^\circ\text{ C.}$  per min.; there were arrests at  $151^\circ\text{ C.}$ ,  $149^\circ\text{ C.}$ ,  $151^\circ\text{ C.}$ , and  $146^\circ\text{ C.}$  respectively. No similar metastable conditions occurred for alloys containing more than 66 per cent. tin, no conditions were obtained at which points on the  $149^\circ\text{ C.}$  line were ever found. Further evidence of the absence of this line is afforded by the absence of a break on the lower boundary of the solid solution of tin in lead. Parravano and Scortecci used this argument also, but when the author plotted their points on the same scale as that of his own diagram he found them to give two straight lines intersecting at an angle of  $21^\circ$  at  $150^\circ\text{ C.}$ , also all the points were lower than his.

According to the diagram of Rosenhain and Tucker an alloy of 13 per cent. tin would be homogeneous at  $150^\circ\text{ C.}$  An ingot was cast on glass, annealed for nine days at  $150^\circ\text{ C.}$ , chilled and polished with benzene and chromic oxide and etched with potassium cyanide. It was a two-phase system with bright patches of the tin rich solid solution. This is consistent with the author's diagram.

The electrical resistance methods of Parravano and Scortecci and of Konno appear to the author to involve the same possibilities of error when applied to the lead-tin system when rods of the alloys are used as were stated by him for the case of the copper-tin system.<sup>5</sup>

### Summary.

1. A continuous method of recording change of electrical resistance as a function of the temperature by means of two Callendar recorders has been applied to the lead-tin system.
2. With precautions adequate to ensure equilibrium the diagram has been found to be of the Roozeboom type 5, without any complication, for temperatures down to  $75^\circ\text{ C.}$
3. The boundaries of the solid solutions of tin in lead and of lead in tin have been found.
4. No line of points has been found at  $149^\circ\text{ C.}$ .

The author is indebted to the Goldsmiths' Reader in Metallurgy, Col. C. T. Heycock, F.R.S., for giving him every facility for making the experiments.

He is also grateful to Mr. E. W. Tremayne, B.A., Emmanuel College, Cambridge, for helping him during the Long Vacation, and to Mr. E. A. G. Liddiard, B.A., Caius College, Cambridge, for his assistance this term.

<sup>5</sup> *Trans. Faraday Soc.*, 1927, 23, 566.

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### DISCUSSION.\*

**Dr. J. L. Haughton** said (*partly communicated later*) that he had read Mr. Jeffery's paper with great interest, as he believed that very valuable work could be done on constitutional diagrams by means of electrical resistivity measurements. One of the great advantages of resistivity measurements over thermal analysis was that the former could be carried out

\* The preceding paper and the same author's earlier paper (*Trans. Far. Soc.*, 1927, 23, 563) were read and discussed together.

## DISCUSSION

extremely slowly so that it was possible to retain the specimen in a state of equilibrium at all temperatures. Mr. Jeffery had, in certain cases, realised these conditions, but there were certain limitations which must be taken into account, and to which reference would be made later.

Dr. Haughton was, however, not satisfied that the method Mr. Jeffery used was altogether desirable. It was very difficult from the description to follow exactly what the *modus operandi* was, but it appeared to consist of measuring, by means of a Callendar bridge, the resistance of a circuit which included the metal under observation and the molybdenum leads dipping into it. Probably compensating leads were used, but it seemed unlikely that these could have been arranged to afford complete compensation. The resistance of the leads must have been many times greater than that of the metal, and the results obtained would undoubtedly be affected by slight variations in the former—variations which one would expect to find in view of the fact that the leads passed from the hot metal in the furnace into the ice flask. The same gradient along the wires at all temperatures could hardly be expected.

The contact resistance between the leads and the metal was also included in the value registered by the bridge. This was likely to be variable and might easily be considerably more than the resistance of the metal, particularly when the experiments were carried out in an oxidising atmosphere. Further, no attempt to check parasite *E.M.F.*'s appeared to have been made. Under certain conditions these might reach a high value.

Again exception must be taken to the use of a large crucible of metal when no attempt was made to keep the change homogeneous by stirring. The method might work satisfactorily above the *liquidus* and below the *solidus*, but, with very slow cooling, segregation was almost certain to occur at temperatures between the *liquidus* and the *solidus*, particularly in the case of metals with such marked differences of density as lead and tin; the conclusion was unavoidable that the composition of the solid lead-tin ingot would be different at the bottom of the pot from what it would be in the neighbourhood of the contacts. As most of the current would be carried by the metal in the neighbourhood of the contacts, this difference was of considerable importance, and the writer would go so far as to say that he believed it might have caused the differences between the results obtained by Mr. Jeffery or Dr. Rosenhain. Mr. Jeffery found that with rapid rates of cooling through the crystallisation interval he obtained an arrest at about  $160^{\circ}$  C., thus agreeing with Rosenhain and Tucker. With very slow rates of cooling he found no sign of this point. If marked segregation occurred, the alloy in the neighbourhood of the contacts might be very much richer in tin than the mean composition of the ingot, and this would probably be amply sufficient to account for the failure to detect the arrest points by the comparatively insensitive method used by Mr. Jeffery. It might also account for the difference in the eutectic composition between Mr. Jeffery's results and those of Rosenhain and Tucker. He felt bound to say that, whatever the explanation, he was not prepared to accept Mr. Jeffery's figure for the eutectic composition in preference to that obtained by the highly accurate work of Rosenhain and Tucker.

With reference to the copper-tin series Mr. Jeffery stated that Isihara's resistance measurements might be untrustworthy because the measurement of resistivity on rods might "not give trustworthy results for heterogeneous conductors in a state of progressive change if it be correct to regard the resistance of such a system as of the nature of a statistical valuation." He (Dr. Haughton) failed completely to understand what was meant by that

sentence, and he would be grateful if Mr. Jeffery would explain it further and show in what way his method overcame this lack of trustworthiness. Isihara's results were in substantial agreement with his (Dr. Haughton's) with reference to the point criticised by Mr. Jeffery, *i.e.*, the existence of a line below the eutectic, except that Isihara showed the line to occur at 180° C. while he showed that it occurred at 189° C. on the copper side and at 186° C. on the tin side of the  $\epsilon$  field. This change of temperature on passing through a homogeneous field was to be expected on theoretical grounds, and he could not see any justification for the statement that the existence of this line involved difficulties in the interpretation of the diagram.

In addition to denying the existence of a line below the eutectic Mr. Jeffery drew the eutectic back to 50 per cent. Sn (35 atoms per cent.) differing in this respect not only from Isihara and the writer, who showed that no eutectic existed when there was less than about 60 per cent. Sn (45 atoms per cent.) present, but also from Heycock and Neville who dotted the eutectic line in the part of the diagram containing less than 65 per cent. (50 atoms per cent.) of tin and showed that tin occurring below this dotted line was metastable.

It would appear that a consideration of the equilibrium diagram would explain these anomalous results. Heycock and Neville showed that the reaction  $\eta + \text{liq.} = \epsilon$ , which takes place in the neighbourhood of 400° C. does not, under normal conditions, complete itself, as the first formed  $\epsilon$  produces a sheath round the  $\eta$  which slows down the rate of reaction enormously. They found that specimens which had been slowly cooled were not yet in equilibrium, after annealing for three weeks, owing to the slowness of diffusion of the liquid through the sheath. In 1915, he (Dr. Haughton) showed that by cooling the alloys from the liquid at a very high rate it was possible to obtain a structure so fine that annealing for a few hours enabled the reaction to complete itself. Mr. Jeffery, on the other hand annealed his specimens for 16 hours in the  $\eta + \text{liq.}$  field, thus growing very large crystals of  $\eta$ . The alloys were then slowly cooled while their resistance was measured. Such alloys when cold would consist of large crystals of  $\eta$  surrounded with thin sheaths of  $\epsilon$  and embedded in areas of solidified liquid (eutectic). They would contain so little  $\epsilon$  that the 180° line (which seemed undoubtedly to be a transformation in the  $\epsilon$ ) would probably not be detectable. The tin rich ones would contain large quantities of metastable  $\eta$  and the copper rich ones large quantities of metastable eutectic. Alloys in this condition would probably require to be annealed for months, if not for years, in order to attain equilibrium conditions. He claimed, therefore, that Mr. Jeffery had not disproved the existence of the 180° line and was not justified in drawing the eutectic line in that part of the diagram containing less than 60 per cent. Sn (45 atoms per cent.). He also submitted that Mr. Jeffery was not justified in claiming that his results are in almost complete agreement with those of Heycock and Neville, as Mr. Jeffery's diagram showed the line H'H'' as extending from 55 per cent. Sn (38 atoms per cent.) to 73 per cent. Sn (58 atoms per cent.) while Heycock and Neville showed it between 60 per cent. (45 atoms per cent.) and 65 per cent. (50 atoms per cent.).

Dr. Haughton was in agreement with Mr. Jeffery when he stated that the  $\eta + \text{liq.} = \epsilon$  reaction occurs at  $411^\circ \pm 3^\circ$ . In his 1915 paper he showed that it occurred at  $415^\circ$ .

**Dr. Rosenhain** (*communicated*) said that although some twenty years had elapsed since he had been concerned with the study of the lead-tin

## DISCUSSION

alloy system, he was naturally interested in any paper dealing with the subject. It would not, of course, be surprising if, after such a length of time, the application of modern methods should require some correction of a diagram published in 1908. There was, however, a tendency to revise the work of older investigators by methods which in themselves were not as accurate as those used in the original work. These "revisions" were apt to pass into the literature as better and more accurate simply because they are more recent, and there were instances where revisions of this kind had led to the acceptance of erroneous data. He was, therefore, inclined to view very critically any attempt to revise the results of work which had been carried out with elaborate care and the fullest possible precautions to ensure accuracy, as was the case with the investigation of the lead-tin system by Mr. Tucker and himself. The methods then used were thermal analysis and microscopic examination carried out with all the experimental resources then available. The composition of the eutectic, in particular, was determined most carefully, the thorough microscopic examination of comparatively large specimens being carried out with a view to securing samples which strictly conformed to the eutectic structure, and these were subsequently analysed. Additional experiments were made by which the last remaining liquid portion of a comparatively large mass of lead-tin alloy was separated, thus fractionating the eutectic from a large quantity of metal. The results arrived at by these separate methods were practically identical, and the results have, therefore, a foundation of careful, accurate measurement, by entirely reliable methods.

Contrasted with these was the electrical resistance method described by Mr. Jeffery. Serious objections existed to the method which he had used, mainly on the grounds that accidental variation in the electrical resistance of his circuit and the occurrence of parasitic electromotive forces might easily introduce serious errors. There was the further difficulty that in a large mass of alloy solidifying very slowly there was certain to be a serious amount of segregation, and unless care were taken to avoid the effects of this segregation, measurements of any physical property upon a small portion of such a mass were apt to give misleading results. In view of these serious objections he thought that it would be unwise to accept Mr. Jeffery's revision of the composition of the lead-tin eutectic as being in any sense more reliable, or even approaching in reliability the original determination by Mr. Tucker and himself.

With regard to the transformation point which was found by his colleague and himself at  $150^{\circ}\text{C}$ . , the position was somewhat different. So far as he could see, Mr. Jeffery simply failed to find this point in the very slowly cooled alloys and therefore concluded that it did not exist. Measurements of electrical resistance, or Mr. Jeffery's method of making them, might be unsatisfactory for determining the lines of an equilibrium diagram. It was by no means certain that every transformation must involve a marked change in electrical conductivity, so that negative evidence from electrical measurements could hardly be regarded as superseding positive evidence from thermal analysis and microscopic examination. On Mr. Jeffery's own results, however, as shown in Fig. 1 of his paper, it appeared that there was at least as much evidence for the existence of a transformation at or near  $150^{\circ}\text{C}$ . as there was against it. He showed the solubility line at the lead end of the diagram as a continuous curve, and cited this as a reason against the existence of a transformation, which would involve the occurrence of a break in this line. Actually he (Dr. Rosenhain) thought that an impartial examination of his plotted point suggested the

occurrence of a break in the curve at the temperature in question. In any case, Mr. Jeffery's results as given in the table afforded no indication of the accuracy of the measurements which he had made. On eleven alloys he recorded the eutectic temperature at  $183^{\circ}$  without any decimals or indication of variation whatever. Was one to conclude that readings were only taken to the nearest degree, and that these eleven readings all agreed within that measure of accuracy—or had the figures been smoothed out in view of the known fact that the eutectic temperature is constant?

**Mr. F. H. Jeffery** in reply said that the Callendar recorder measured changes of electrical resistance during heating and cooling; these changes were due partly to the molybdenum wires and partly to the alloy. The usual method of compensation was arranged for the copper leads from the ice junctions of the molybdenum wires to the recorder, but there was no compensation for the varying resistance of the molybdenum wires; their resistance, however, varied continuously, and the rapid changes of resistance due to the formation of new phases in the alloys were found to be not masked. Numerous experiments made with pure metals showed that their freezing-points could be found to within  $\pm 0.2^{\circ}$ ; for alloys, heating curves and cooling curves gave identical results which could be found again when the experiments were repeated. He thought that this showed that serious errors could not have been caused by parasitic *E.M.F.*'s and contact resistances. Every portion of the alloy must have contributed to the change of resistance measured; he did not see any justification for assuming that most of the current was carried by metal in the neighbourhood of the contacts. He preferred a large mass of metal in a crucible to a thin rod: the quantity of current carried by a thin layer of metal at the bounding surface of the alloy was a much smaller fraction of the total current in the former case than in the latter; the stresses due to changes in density when a new phase is formed must have a greater effect in the latter than in the former. He thought that the degree of segregation postulated by Dr. Haughton and Dr. Rosenhain could hardly be consistent with fact. In the copper-tin series he found the isothermal line corresponding with  $\eta + \text{liquid} \rightleftharpoons \text{H}$  to be at  $411^{\circ} \pm 3^{\circ}$ ; Dr. Haughton found  $415^{\circ}$ . Was it possible that these two results should be so nearly the same if his (Mr. Jeffery's) work were vitiated by the effects of segregation, by parasitic *E.M.F.*'s and by contact resistances? For finding points on the copper-tin eutectic isothermal the alloys were slowly cooled through the  $\text{H}'\text{H}$  temperature as stated in the paper, then more rapidly until a temperature of about  $20^{\circ}$  above the eutectic temperature was reached, then annealed for about sixteen hours, and then slowly cooled through the temperature. Points were found on the eutectic line for the alloys 40, 48, 55 atomic per cent. tin. In Fig. 4 these points were joined by a continuous line to the point for the 60 atomic per cent. alloy; he regretted that he did not correct this in the proof, he intended to leave these points in isolation, being aware of the results that Heycock and Neville had obtained by long annealing. As to the Isihara line he would emphasise what he stated in his paper, that the question is worthy of further investigation. The temperature of the lead-tin eutectic isothermal was found to be  $183^{\circ} \pm 0.3^{\circ}$  for the eleven alloys examined.

He hoped to experiment with other alloys with a view to examining the applicability and limitations of his method.

## MODIFICATIONS OF THE SAND AUXILIARY ELECTRODE.

BY THOMAS BROOKS SMITH.

(Received 13th December, 1927, and read before the Society,  
25th January, 1928.)

The value of the Sand electrode<sup>1</sup> is generally recognised for accurately controlling the potential drop at the cathode during separations of metals, the oxidation potentials of which are very close to one another or to that of hydrogen. Where such electro-analytical work is only carried out intermittently in a laboratory equipped primarily for physico-chemical work the original arrangement leaves but little to be desired. If, however, equipment is to be obtained specially for work of this nature, it is obviously worth considering whether one instrument may be made to serve both as voltmeter and null point detector, but a difficulty is encountered in connection with the high resistance of the usual type of half-cell which would necessitate the use of an extremely sensitive and therefore costly voltmeter. Means have been found of reducing the resistance of the auxiliary electrode circuit without introducing sensible errors on account of concentration polarisation in the standard half-cell. The dual use of the voltmeter which thus becomes possible has the double advantage of considerably reducing expense and providing an exceptionally convenient means of observing the null-point.

A rough determination of the resistance of the various parts of an electrode of the design shown in Fig. 1, fitted with a Sand pattern tap<sup>2</sup> (Fig. 1a), was carried out in the usual way with the aid of a Wheatstone bridge using alternating current. The results obtained were as follows:—

TABLE I.

	Resistance in Ohms.	
	When whole of Apparatus is at 18° C.	When end of Connecting Tube is Immersed in a Bath at 90° C.
Tube between A and B containing Hg <sub>2</sub> SO <sub>4</sub> in 2 <i>N</i> H <sub>2</sub> SO <sub>4</sub> .	700	
Tap (resistance very variable).	12,000	12,000
Tube between B and C containing <i>N</i> Na <sub>2</sub> SO <sub>4</sub> .	3,000	
Tube between C and E containing <i>N</i> Na <sub>2</sub> SO <sub>4</sub> .	6,000	2,000
Total	21,700	14,000

<sup>1</sup> H. J. S. Sand, *J.C.S.*, 1907, 91, 373.

<sup>2</sup> This type of tap is used without a lubricant. Small quantities of liquids from the adjacent tubes are retained by capillary forces between the tap plug and its socket. The film thus formed affords the only electrical connection between AB and BC.

### Early Modifications.

*Pattern shown in Fig. 1.*—The reasons which make the use of diaphragms unsuitable for very accurate potential measurements are of small weight when an order of accuracy of only 0·01 volt is concerned, and in the first modification attempted the special tap (Fig. 1a) was replaced by an ordinary three-way tap containing a filter paper diaphragm (Figs. 1b and 2). This consisted of two thicknesses of Whatman's No. 50 filter paper, cut slightly larger than the hole in the tap and rammed tightly into it. If this type of apparatus were to be adopted for routine work it would doubtless be desirable to find some more permanent way of fixing the diaphragm, but the method adopted was found to be adequate for the purposes of preliminary experiments, the apparatus remaining in working order for at least two or three months. The resistance of the diaphragm is only of the order of 50 to 100 ohms and the total resistance of the electrode when the capillary tube is immersed in a bath at 90° is reduced to about one-third of that of the original pattern.

The modified electrode was tested by carrying out a series of bismuth estimations during the course of which the sensitivity of the means adopted

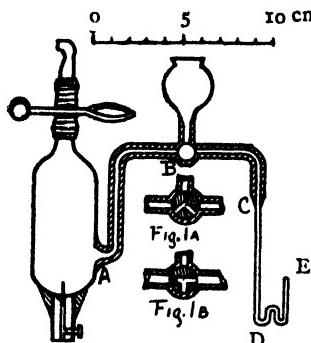


FIG. 1.

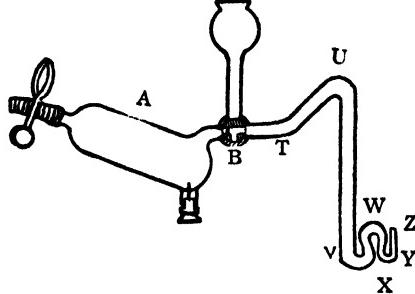


FIG. 2.

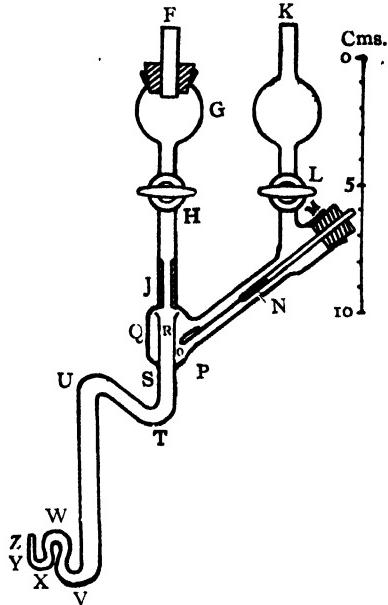
for the null point detection was determined when the fairly sensitive voltmeter referred to as No. I. was employed. The characteristics of the instrument are given below, Table II. The circuit arrangements are shown in Fig. 4 from which it will be seen that when the switch S is to the right the instrument serves for the detection of the null point, and with the switch to the left for the measurement of the potentiometer voltage. It will be seen from the Table that a deviation from the null point of one scale division (about 0·75 mm.) is equivalent to a difference of potentiometer voltage of 0·15. Since the minimum deviation which can be detected with ease is about one-fifth of a division, such an arrangement would enable the potential to be controlled to within 0·03 volt. With great care such an arrangement might possibly be used but is hardly to be considered satisfactory.

*Pattern shown in Fig. 2.*—Except near the extreme end the connecting tube is of wide bore. The form of the portion between T and Z is similar to that of the corresponding part in the Fig. 3 pattern and will be discussed later. The connecting tube to the left of the tap is made as short and wide as practicable, thus avoiding the quite unnecessary resistance caused by the tube AB in the original pattern. The possible risk of the electrolyte concentration being affected by diffusion of the connecting liquid from B was

shown to be negligible, and since a lubricated tap may be employed, diffusion can be stopped altogether during periods when the electrode is not in use. Furthermore, the use as a connecting liquid of sulphuric acid of the same concentration as that employed in the preparation of the half-cell electrolyte is usually permissible; its employment not only reduces the resistance still further but also enables this type of electrode to be used for some months without refilling with electrolyte.

If this pattern is used in conjunction with voltmeter I a change of 0.01 volt in the potential drop at the cathode causes a null point deflection of a quarter of a scale division when  $N$  sodium sulphate is used as connecting

FIG. 3.



The joining of the small bore tube J and the bulb Q requires careful workmanship if the downward passage of liquid from J to R is to leave the electrolyte in Q undisturbed. This, however, is only of importance when the connecting liquid is less dense than the electrolyte, and if the auxiliary cell is to be used under these conditions it is advisable to test it in the following way. The entire apparatus except the thistle funnel G is filled with electrolyte, and G is then filled with connecting liquid which should be coloured with a suitable dye; the tap H is then opened and the flow of this liquid is observed in the neighbourhood of J. Generally, however, liquids of high specific gravity are to be preferred for use in the connecting tube, and under these conditions the junction is arranged near S. The form and dimensions of the gap between J and R are not then critical, and in any case the resistance of the gap is comparatively insignificant.

After the introduction of a little mercurous sulphate paste i. to the pocket in the amalgamated platinum foil the latter is placed in the tube MP. Electrolyte is then introduced by applying suction at K whilst the end Z is immersed in the liquid, the tap H being closed and L open. In cases where

the connecting liquid is less dense than the electrolyte the excess of the latter is allowed to run out of the tube RTZ by opening the tap H. Connecting liquid may then be drawn up into G through Z by applying suction at F. When, as is usually the case, the liquid is denser than the electrolyte the end Z should be immersed in the former immediately after the electrolyte has been sucked up, but without first removing it from RTZ as in the former case. Suction is then applied at F and the tap H cautiously opened until the connecting liquid is drawn up to a point about 2 cms. above the bend T, after which the tap is again closed. This operation may be carried out most conveniently when the tube TU is horizontal. To enable the junction of the two liquids to be seen readily it is advantageous to colour the connecting liquid with a suitable dye. Brilliant cresyl blue was used in most of the experiments described.

liquid. Such an arrangement is quite sensitive enough for practical purposes. If dilute sulphuric acid is employed as connecting liquid, the deflection corresponding to a potential change of 0.01 volt can readily be seen when the null point instrument is viewed from a point several feet away.

#### The Pattern finally Adopted.

In the course of experiments to ascertain whether a less sensitive control instrument could be employed, it seemed desirable to make a further substantial reduction in the resistance of the auxiliary electrode circuit. Since it was not found practicable to achieve this by further modification of the

design attention was next turned to the possibility of utilising connecting liquids of high conductivity such as concentrated ammonium sulphate solution or maximum conductivity sulphuric acid. The pattern last described was not regarded as suitable for connecting liquids of higher S.G. than the half-cell electrolyte, and the pattern shown in Fig 3 was designed to permit of the use of connecting liquids of any desired density. Since no use is made of a diaphragm the relative permanence of the former pattern is sacrificed, but in practically all other respects the newer pattern was found to be preferable.

The electrode O (Fig. 3) consists of platinum foil amalgamated electrolytically before introduction into the apparatus. The end of the foil is turned up to form a pocket into which is placed a small quantity of mercurous sulphate paste. If a connecting liquid were used of specific gravity less than that of the electrolyte, the junction of the two liquids should occur in the annular space between the tube R and the bulb Q. As a rule, however, connecting liquids are used which are denser than the electrolyte, and in such cases the junction should occur in the neighbourhood of S.

*Influence of Convection Currents.*—The connecting tube is almost invariably immersed in a hot liquid and this sets up convection currents in the tube UV (Fig. 3). It is obviously undesirable that these currents should reach the junction between the connecting liquid and the electrolyte and to obviate such a difficulty, the tube TU (Figs. 2 and 3) is inclined as shown in the diagrams. It also follows from consideration of this convection current, that the sinuous tube between V and Z should be long enough to prevent any appreciable amount of the metal to be estimated from reaching the point V. If attention is paid to this, it is advantageous to use a fairly wide tube between U and V since the heating up of the contained liquid causes the expulsion of a considerable amount of the connecting liquid, and this helps to render superfluous the washing out of the connecting tube during the course of an estimation.

The following data show the extent and persistence of this expulsion effect:—

Time . . .	1	2	4	8	15 mins.
Vol. expelled .	0.07	0.85	0.95	0.115	0.135 c.cs.

It will be seen that even after the first minute the rate of expulsion is considerable in comparison with the volume of the last centimetre length of the capillary (Y to Z, Fig. 3), which is 0.025 c.c.

*Diffusion Effects.*—Whilst the design of the tube between V and Z was under consideration diffusion effects were studied either by placing the connecting tube filled with a suitable indicator into a bath of acid or alkali, or alternatively by filling the tube with water and placing in a bath of potassium permanganate. No attempts were made to measure exact rates of diffusion since the phenomenon in question is complicated by other effects such as the irregular shape of the tube and the influence of stirring. All that was attempted was to design a connecting tube having as low a resistance as possible, but in which diffusion effects would be negligible even for such substances as acids and uni-univalent salts which have higher diffusion coefficients than the salts of the bi- and ter-valent metals involved in most estimations.

As a result of the diffusion experiments it was concluded that the common practice of washing out the connecting tube during the course of an estimation is quite unnecessary. The upper limit of the errors that may

be introduced by omitting this precaution were roughly assessed in the cases of the following representative estimations :—

(1) *Bismuth*.—If 0·3 gram of the metal is to be deposited from 100 c.cs. of solution, and the current at the outset is 3·4 amperes, then about 75 per cent. of the bismuth is deposited by the end of the second minute, and 90 per cent. by the end of the third. In 3 minutes the relatively fast moving hydrochloric acid does not penetrate more than two or three millimetres into the capillary, and the volume of this portion of the tube is about 0·005 c.cs. Even if the bismuth concentration throughout this volume were the same as that of the bath before the commencement of the deposition the amount lost would amount only to 0·000,015 gram, an amount not weighable on an ordinary analytical balance. In reality the amount lost during the first three minutes would be considerably less than this, and the further loss during the remainder of the experiment would be still more insignificant.

(2) *Nickel in the Presence of Zinc*.—In this case the time required for the deposition is considerably longer, and there is not the same tendency for the greater part of the metal to be deposited during a small fraction of the total period. Against these factors which tend to increase the loss by diffusion must be placed the fact that the volume of solution employed (250 to 300 c.cs.) is considerably larger than those used in the bismuth estimation. During the 15 minutes required for the practically complete deposition of nickel, diffusion effects are only perceptible to a depth of 8 millimetres in the capillary tube, and the volume concerned is 0·02 c.cs. Even if this represented loss of nickel solution of the original concentration, the resulting error would only be about 0·007 per cent and the weight of nickel lost 0·000,01 gram.

*Feasibility of Employing Connecting Liquids of High Conductivity*.—The following possible sources of error were considered: (i) alteration of the deposition bath; (ii) alteration of the half-cell electrolyte; (iii) concentration polarisation of the half-cell owing to the relatively heavy currents which may pass through it; (iv) variation in diffusion potentials at the liquid junctions. Concerning (i) it has been shown that washing out of the connecting tube is unnecessary and that the total amount of connecting liquid otherwise expelled when the connecting tube is immersed in a bath at 90° is of the order of 0·16 c.cs. in half an hour. Even when maximum conductivity sulphuric acid (*circa* 7·5 N) is employed, this small amount would not as a rule cause any undesirable change of hydrogen ion concentration even in an alkaline electrolyte. In this connection it should be remembered that in all cases where acidity is a critical factor buffer solutions are invariably employed as electrolytes. Doubtless, however, it would be safer in such cases to employ either weaker sulphuric acid or a solution of a neutral salt such as ammonium sulphate.

To test whether the use of maximum conductivity sulphuric acid in the connecting tube could lead to appreciable alteration in the half-cell electrolyte, the electrode vessel was filled with sulphuric acid of  $\rho_H$  value 0·9 coloured with brilliant cresyl blue, and the maximum conductivity acid was also coloured with this indicator. The junction between the two liquids occurred at the point S (Fig. 3). The connecting tube was placed in a bath at 90° for half an hour and then allowed to remain at the laboratory temperature for 9 hours. At the end of this period the junction was still quite sharp and no perceptible change of colour had taken place in the electrode vessel. This test showed that if any change at all had taken place it was less than 0·2 in the  $\rho_H$  value. Even if the change had

been as large as this the effect on a hydrogen or quinhydrone electrode, in which the potential is directly dependent on  $p_H$  value, would amount only to about 0.01 volt. In the case of a Hg-Hg<sub>2</sub>SO<sub>4</sub> half-cell any change in the sulphuric acid concentration is only of importance in so far as it affects the solubility of mercurous sulphate, and this influence is inappreciable.

It may be concluded that with the aid of connecting liquids of high conductance the resistance of the auxiliary electrode circuit can be reduced sufficiently to permit of the use of an instrument of moderate sensitivity, such as the voltmeter referred to as No. II (Table II.), provided that the potential of the auxiliary cell remains constant under the working conditions.

### Polarisation Tests on the Auxiliary Cell.

The half-cell to be tested was used in conjunction with a Bi-Bi + + + half-cell formed by interrupting a bismuth estimation a minute or two after switching on the current. Various initial demands were made from such a cell by a suitable adjustment of the potentiometer. The variation of current with time was noted in each of these cases and typical results are shown by the curves in Fig. 7.

*Curve (a)* relates to an auxiliary cell containing mercury in contact with a saturated solution of mercurous sulphate in 2*N* sulphuric acid, but in which no solid mercurous sulphate was present. It will be seen that such a cell is incapable of supplying the current necessary to give an appreciable deflection on voltmeter II, though it would be adequate for use with voltmeter I.

*Curve (b)* refers to a half-cell similar to that shown in Fig. 3 except that the solid mercurous sulphate was placed in the bottom of the bulb Q instead of in a pocket in O. It will be seen that this arrangement is only slightly better than that in which no solid is present, and decidedly inferior to the Fig. 3 pattern to which the remaining curves refer.

*Curve (c)* shows that the recommended form of auxiliary cell is capable of functioning under a load of 0.3 milli-amperes for at least a quarter of an hour without showing signs of polarisation. This current gives a scale deflection of two divisions on voltmeter II. In practice there is never any need for the deviation from the true null point to exceed one scale division, and without much difficulty the variation could be kept within still smaller limits. A deviation of two divisions would be quite exceptional. Hence the electrode shown in Fig. 3 is quite capable of being used in conjunction with voltmeter II.

*Curves (d) and (e)* show that polarisation effects might be encountered if a voltmeter were employed, the sensitivity of which is much less than that of pattern II.

The adequacy of the auxiliary electrode shown in Fig. 3 for use in conjunction with voltmeter II was further tested by frequently checking the potential of the half-cell immediately before and after use. The maximum variation observed was 0.0026 volt. This shows that the combined effects of polarisation, variation of diffusion potentials, and minor variations of temperature, are practically negligible.

### Results.

*Use as a Quinhydrone Electrode.*—The Fig. 3 pattern serves excellently as a quinhydrone electrode if a strip of plain platinum be substituted for

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**TABLE II.—COMPARISON OF VARIOUS PATTERNS OF AUXILIARY ELECTRODES.**

Containing Hg in contact with a saturated solution of  $Hg_2SO_4$  in  $2N H_2SO_4$ .  
The figures in the last two columns were obtained during the course of a bismuth estimation.

Pattern.	Liquid in Connecting Tube.	Resistance.		Difference of Potentiometer. Voltage $\equiv$ 1 Division. Deviation from Null-point	
		Whole of Apparatus at $18^\circ C.$	Connecting Tube Immersed in Bath at $90^\circ C.$	Voltmeter I.	Voltmeter II.
Sand.	$N Na_2SO_4$	ohms. 22,000	ohms. 14,000	volts. 0.4	—
	$2N H_2SO_4$		3,500	—	—
	$N Na_2SO_4$	10,000	4,000	0.15	—
Similar to Sand but with tap shown in Fig. 1a.	$N Na_2SO_4$	4,000	1,300	0.035	0.2
	$2N H_2SO_4$	550	350	0.01	0.05
	$N Na_2SO_4$	4,000	1,300	0.035	0.2
Fig. 2.	$2N H_2SO_4$	550	350	0.01	0.05
	$7.5N H_2SO_4$	270	150	0.006	0.03
	$8N Am_2SO_4$	850	420	0.01	0.06

**DATA CONCERNING THE VOLTMETERS EMPLOYED.**

	Voltmeter I.	Voltmeter II.
Sensitivity in ohms per volt	500	134
Current in milli-amps. for full scale deflection	2	7.5
No. of scale divisions		
Distance between scale divisions near zero end of scale	One 75 and one 50 division scale 0.75 and 1 mm.	50 0.9 mm.
Ranges		
Voltmeter resistors (V.R. in Figs. 4 and 5)	Multi-range inst. for use with external multipliers. The 2.5 volt range was used for the experiments here described 1,200 ohms for 2.5 volt range	1 and 2.5 volt.
Resistance of moving coil only	50 ohms	91 and 292 ohms.
		43 ohms.

**TABLE III.**

**SATISFACTORY RESULTS WERE OBTAINED FOR THE FOLLOWING ESTIMATIONS.<sup>3</sup>**

Estimation.	Volt- meter.	Electrode Shown in	Nature of Half-Cell.	Connecting Liquid.
Bi	I.	Fig. 2	Hg— $Hg_2SO_4$ in $2N H_2SO_4$	$N Na_2SO_4$
"	I.	Fig. 3	" " " "	Max. cond. $H_2SO_4$ (S.G. 1.223)
"	II.	"	" " " "	$0.9 N Na_2SO_4$
"	I.	"	Quinhydrone $0.1 N H_2SO_4$	$0.1 N H_2SO_4$
Ni in pres. of Zn	II.	"	Hg— $Hg_2SO_4$ in $2N H_2SO_4$	$8 N Am_2SO_4$

<sup>3</sup> A rotating anode and Sand pattern cathode were used in each case. For details of procedure see Sand, *J.C.S.*, 1907, 91, 373, concerning the bismuth estimation, and A. Fischer, *Chem. Ztg.*, 1908, 32, 185, concerning the separation of nickel and zinc.

the amalgamated piece. Such a half-cell works admirably in conjunction with Voltmeter I. Difficulties are encountered in trying to adopt the quinhydrone for use with a less sensitive voltmeter and these are at present under investigation. The use of  $0.1N$   $H_2SO_4$  together with  $0.9N$   $Na_2SO_4$  is recommended as a connecting liquid; high concentrations of  $H_2SO_4$  are not available since they lead to the decomposition of the quinhydrone. The potential of the quinhydrone electrode in  $0.1N$   $H_2SO_4$  is  $0.032$  volts less than that of the  $Hg-Hg_2SO_4$  in  $2N$   $H_2SO_4$  electrode generally recommended for electro-analytical work.

### The Electrical Apparatus used.

The layout of the electrical apparatus is shown in Figs. 4 and 5. A considerable use is made of the better class of radio apparatus the compact design of which greatly facilitates the enclosure of the parts most vulnerable to attack by the "atmosphere" of a chemical laboratory.

The usual type of single range voltmeter contains within the case a fixed resistance in series with the moving coil, and it is necessary to insert between them a tapping leading to a third terminal in order to adapt such an instrument for use in the circuits shown. Most multi-range instruments designed for use with external volt multipliers do not require any alteration. Some multi-range voltmeters fitted with enclosed resistors have terminals which include only the moving coil in the circuit, but other patterns necessitate the addition of an extra tapping.

On reference to Fig. 4 it will be seen that when V is used as a voltmeter to measure the potential between D and F a small current necessarily flows through VR, and this may be appreciable compared with the current flowing in AC when a high resistance radio pattern potentiometer is employed. Hence VR should remain in parallel with AC even when V is being employed to determine the null point. Theoretically the removal of V from the circuit DVRF will affect the potential between A and C, but with resistances of the order shown the change will be less than  $0.01$  volt.

This will no longer be true if a less sensitive voltmeter is used for which VR may perhaps be of the order of  $100$  to  $300$  ohms. In such a case the potentiometer should have a much lower resistance. Most radio pattern rheostats of about  $30$  ohms resistance are fitted only with two terminals, but it is an easy matter to add a connection to the free end of the resistor and though the potentiometer so formed is only capable of altering the voltage by a series of steps nevertheless these steps are small enough to admit of the adjustment of the potential to within  $0.01$  to  $0.02$  volt. The manipulation of the apparatus will, however, be greatly facilitated if two rheostats are placed in series, one having a resistance of about a quarter of that of the other, and serving as a fine adjustment. During the course of an estimation it is usual to allow the cathode potential to rise by

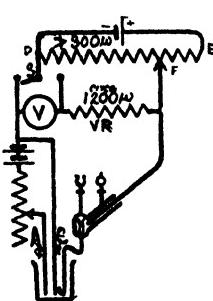


FIG. 4.

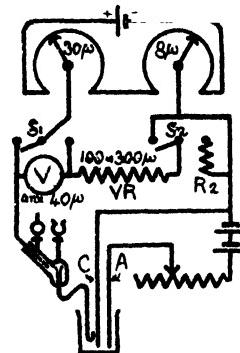


FIG. 5.

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about 0.2 to 0.3 volt, and such a change will be brought about by rotating the knob of the fine adjustment through about  $180^\circ$ .

A second modification which becomes necessary when the resistance of VR is relatively small arises from the fact that the resistance of V is no longer negligible in comparison with that of VR. In these circumstances a switch  $S_2$  should be introduced which throws into the circuit a resistance  $R_2$  equal to that of V when the latter is removed from the circuit by means of switch  $S_1$ . In practice, both  $S_1$  and  $S_2$  are incorporated in one double pole double throw switch preferably of the panel mounting type.

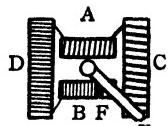


FIG. 6.

If at the commencement of an estimation the voltmeter is switched into circuit as a null point detector before the main current is roughly adjusted, the pointer will be driven hard against the left-hand stop which should therefore be of a resilient nature. If a very sensitive instrument is employed it is advantageous for the stop to short circuit the moving coil.

It is obviously advantageous to enclose all switch and rheostat contacts, and in the actual apparatus described the control-box included not only the switch just mentioned and the potentiometer resistors, but also the main circuit switch and rheostat.<sup>4</sup> The latter must be capable of carrying from 3 to 4 ampères at the commencement of an estimation and the ordinary radio patterns are too light to serve for this purpose. On the other hand a 15 or 20 ohms resistance of the ordinary laboratory type entirely wound with wire capable of carrying 3 to 4 amperes is unnecessarily cumbrous, since heavy duty wire is only essential up to a value of 3 or 4 ohms.

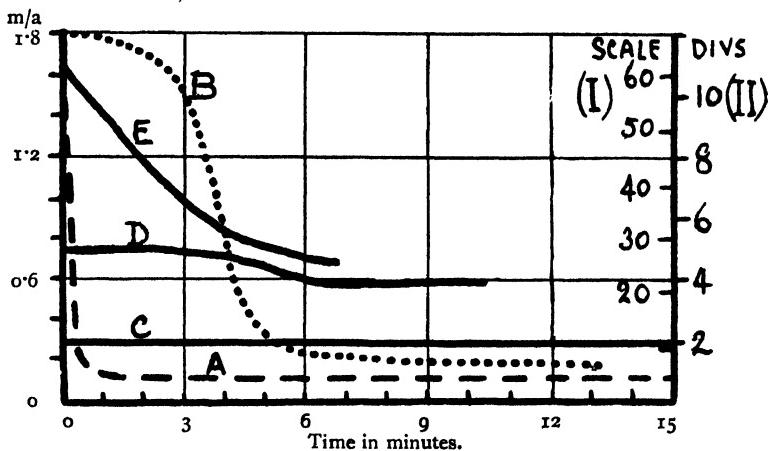


FIG. 7.

To combine compactness with adequate current carrying capacity it is desirable either to use a rheostat consisting of sections wound with wire of several different thicknesses,<sup>5</sup> or alternatively, to arrange that two or

<sup>4</sup> When the main circuit rheostat is enclosed in a box it is desirable that the latter should be provided with a door or flap which can be opened during estimation to ventilate the rheostat and closed when the apparatus is not in use. It is advantageous to include in the box a small vessel containing soda lime to absorb acid fumes.

<sup>5</sup> A very satisfactory form of rheostat was made by adding two coils C and D (Fig. 6) to a commercial radio pattern dual rheostat consisting of a rotating copper arm moving over two coils A and B. A longer contact arm must of course be fitted, and a portion of the wire on the existing coil B must be removed to make room for the stop F.

more resistors may be put in parallel for low resistances or in series for high.<sup>6</sup>

### Summary.

(i) By the use of a porous diaphragm in place of the special tap of the Sand electrode, and by modifying the design of the tube, it has been found possible to reduce the working resistance of the auxiliary electrode to about one-tenth of the usual value. This enables the potentiometer voltmeter to function also as a null point detector without causing any appreciable error on account of concentration polarisation of the half-cell.

(ii) A second modification is described in which the use of either taps or diaphragms in the electrical circuit is avoided. It has about the same resistance as the first pattern but permits of the use of connecting liquids of higher conductivity than usual. This brings the null point detection within the range of a voltmeter of relatively low sensitivity. For most purposes this modification is to be preferred, but the diaphragm pattern has the advantage that it may be used for a considerable time without refilling with electrolyte.

(iii) The employment of a voltmeter for the detection of the null point is more convenient than the use of a capillary electrometer and the cost of the latter is saved.

(iv) The second modification can conveniently be employed as a quinhydrone electrode, the use of which has been shown to be effective in, the control of bismuth estimations.

(v) Arrangements are described for utilising, and, where necessary, modifying panel-mounting radio apparatus so as to permit of the enclosure of the parts most vulnerable to attack by acid fumes.

<sup>6</sup> Such an arrangement is commercially obtainable, the two resistors being operated by a single control knob. This requires less alteration to adapt it to the present purposes, but it is unfortunate that the current carrying capacity is barely sufficient. The coils in parallel will certainly not take 3 amperes for any appreciable length of time, but it is nevertheless possible to utilise this rheostat for an estimation such as that of bismuth in which the current of the order of 3 amperes only persists for about a minute, rapidly falling in the course of a few minutes to less than an ampere. Obviously it would also serve for the estimation of nickel in the presence of zinc, since in this instance the current is never required to exceed 1 ampere.

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## OVERPOTENTIAL AT METALLIC CATHODES. SILVER IN NEUTRAL AND ALKALINE SOLUTIONS.

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The present research is one of a series that is being carried out, on the suggestion of Dr. H. Sand, on the relation between polarisation during the passage of a current, and on other factors. Those principally to be considered are the nature of the electrolyte and of the cathode. Previous

work<sup>1</sup> has shown that when cathodes are polarised with increasing current densities and the polarisations or overpotentials are measured by the so-called "commutator" method at definite intervals after breaking the current, well-defined maxima are obtained in all cases. The values found depend on the time intervals, which should therefore always be stated, and measurements have been carried out for intervals down to  $1.1 \times 10^{-4}$  seconds after the breaking of the current. When the polarisations are measured during the passage of a current by the so-called "direct" method, no such maxima are obtained, but in nearly all cases inflexions or abrupt changes in direction in the polarisation-C.D. curves are observed, and these appear to be related to the maxima found by the commutator method.

In the work to be recorded polarisation-data of the type just described have been determined for silver cathodes in solutions of neutral and alkaline electrolytes.

*Preliminary Experiments.*—Difficulties were experienced at first in obtaining reproducible results, particularly in fairly strong sodium hydroxide solution, and these were traced in every instance to the formation of a spongy, black deposit which appears to be produced particularly readily where local high C.D.'s have been used. When working by the commutator method steady rises in the overvoltage took place with increase of time and C.D. which were not reproducible and were specially marked when successive experiments on the same solution were carried out. At the same time a considerable quantity of the black deposit was produced on the cathode, in the solution, and even on the anode. When this was removed the variations were less marked. It was found that the use of a cylindrical platinum anode which entirely surrounded the whole cathode portion of the apparatus removed these difficulties, due presumably to the production of a uniform C.D. on the electrode. It was thus found necessary to remove all traces of deposit from the apparatus between experiments. The effect is independent, within limits, of the purity of the solution used. The results are further stabilised if the solution is stirred by a stream of hydrogen bubbles, and the effect of oxygen from the anode is minimised by placing the latter well above the cathode.

Besides the arrangement of the anode, the preliminary treatment of the cathode is of great importance. Other conditions being equal, reliable results can always be obtained if the silver is mechanically scraped and polished bright at the beginning of an experiment. A tarnish barely visible to the naked eye is sufficient to cause a slight rise in the overvoltage, and this effect is cumulative with time.

With a clean, fresh electrode, the times and C.D. required to produce a constant value of the over-voltage are reproducible, but in no other case. A used cathode which gave abnormal results behaves similarly when placed in a fresh solution, and in general, these remarks apply also to the direct method.

*Examination of the Deposit.*—A solution of 2*N* sodium hydroxide was electrolysed with intermittent current under conditions tending to produce a large quantity of deposit. A deposit was observed on both electrodes and on the bottom of the vessel, and was examined under the microscope by reflected light, with a  $\frac{1}{4}$ -inch objective. Where the deposit was thick on the cathode, the surface was so roughened that no definite form could be assigned to it. Where it was thinner the roughness was seen to be due to

<sup>1</sup> Sand, Grant, and Lloyd, *J. Chem. Soc.*, 1927, 129, 378. (Results of other workers are also discussed here.)

large and small craters having the appearance of burst blisters. These covered the whole of the surface of the silver, and were oriented in parallel lines, presumably as a result of the electrode having been scraped in one direction during the preliminary treatment. The deposit in the beaker appears to have been derived from that on the cathode. It took the form of a conglomerate of black masses. The anode deposit was similar in character to that on the cathode, but was much less in quantity, and was made up of smaller craters. Since it was produced both inside and outside the platinum cylinder to equal extents, it cannot have been transferred mechanically from the cathode. All the deposits could be easily isolated. They were well washed with hot distilled water, dried and examined. They were all found to give the reactions of silver.

Similar effects were also noticed with some of the other electrolytes (particularly with disodium hydrogen phosphate, potassium chloride and sodium sulphate), but in these cases they were less marked.

So far as the dependence of overvoltage on the method of measurement, time, and C.D. is concerned, the behaviour of a silver cathode is similar to that of one of antimony.

The cathode was a solid cylinder of the purest silver obtainable, 1·4 cm. in length and 3 sq. cm. in area. The electrolytes used are shown in Table I., the concentrations stated being approximate. In the majority of cases the chemicals were the purest obtainable, tests for common impurities giving negative results. As is indicated above, however, the purity of reagents had, in general, little influence. The apparatus was the same as that previously described.

### Results.

*Variation of Overvoltage with Time.*—The overvoltage was read immediately after the commencement of electrolysis and subsequently after regular intervals of time. Table I. shows some of the results. The over-

TABLE I.

Solution.	C.D. Millamps. per cm. <sup>2</sup> .	Time (min.).						
		0.	5.	15.	20.	30.	45.	60.
2 <i>N</i> . NaOH . .	70	280	350	400	410	435	455	455
<i>N</i> . NaOH . .	20	410	427	433	435	440	450	460
Ca(OH) <sub>2</sub> (sat.) . .	30	350	410	460	490	493	497	—
Ca(OH) <sub>2</sub> (semi-sat.) . .	30	480	520	510	510	515	—	—
Ba(OH) <sub>2</sub> (sat.) . .	30	400	455	435	435	437	437	—
<i>N</i> /37. NEt <sub>4</sub> OH . .	30	490	520	550	550	555	550	550
<i>N</i> /40. NMe <sub>4</sub> OH . .	3	410	425	435	430	430	435	435
<i>N</i> . Na <sub>2</sub> CO <sub>3</sub> . .	40	340	505	505	505	505	505	—
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> (semi-sat.) . .	30	680	690	695	690	688	—	—
<i>N</i> . HNa <sub>2</sub> PO <sub>4</sub> . .	{ 5 100 300	617 680 660	625 670 665	637 663 668	640 665 670	645 667 670	645 667 —	—
<i>N</i> . Am <sub>2</sub> CO <sub>3</sub> . .	30	450	560	720	720	720	720	720
<i>N</i> /2. Am <sub>2</sub> CO <sub>3</sub> . .	30	440	550	720	720	720	720	720
<i>N</i> . Na <sub>2</sub> SO <sub>4</sub> . .	30	775	780	780	780	780	780	—
<i>N</i> . KCl . .	30	900	880	885	890	890	890	—

*Note.*—In the case of *N* sodium hydroxide the overvoltage attained the value 460 millivolts after 50 mins. and remained constant for a further 50 mins. This result was subsequently confirmed.

voltages are given in millivolts, and represent the potential-differences between a reversible hydrogen electrode and the working electrode in the same solution. They are average values during  $6.7 \times 10^{-4}$  secs., the current running for  $13.4 \times 10^{-4}$  secs.

It will be noted that a fixed value of the overvoltage is attained, for a particular C.D., after a certain time for each electrolyte, and that this value remains constant for a considerable period. The time taken to arrive at this value decreases as the electrolytes approach the neutral-point. In the case of neutral solutions it is only a few minutes. The phenomenon is independent of the C.D., as shown in the case of *N*. sodium phosphate, except with regard to the final constant value attained (see Table II).

*Variation of Overvoltage with Current Density.*—The overvoltage was read at various cathodic C.D.'s, time being allowed in each case for the overvoltage to assume its constant value as shown in Table I. Once the constant value had been attained for the first reading, the current was altered, without interrupting the electrolysis, for the second reading, and the time required for the constant value to be attained was thereby much reduced.

In general the results were obtained in the order of decreasing C.D.'s, as the experimental errors were less if the current ran only for a short time, especially in the case of strongly alkaline solutions. Apart from this, results obtained in order of increasing C.D. were the same as those found for decreasing C.D. Measurements were made by the direct method by short-circuiting the commutator across two of its poles so that the current became continuous. In these experiments the tube (A in Fig. 1) connecting the electrolyte with the hydrogen electrode (B) was drawn out to a capillary, which was bent at right-angles so as to fit into a hole drilled in the silver cathode D. The end of the capillary-tube was flush with the electrode at the point where it emerged, and the waste hydrogen from the hydrogen electrode was bubbled across the exit, by means of the tube C, so as to keep it clear from minute bubbles of electrolytic hydrogen. This was found to have a marked effect in stabilising

the overvoltage. Readings were taken by the direct and commutator methods both alternately and consecutively. In all cases consistent and reproducible results were obtained independently of whether the readings were made with increasing or decreasing current densities. Some of the results are shown in Tables II. and III.

The results indicate the following conclusions:—

(1) Above a certain C.D., which we have designated the "critical C.D." and which is shown in Table III., the overvoltage measured by the commutator method remains constant. Below this value it increases rapidly with the C.D.

(2) The overvoltage measured by the direct method increases rapidly with the C.D. for low values of the latter, but increases at a lesser rate when the higher values are obtained. Between these points a distinct change of direction or point of inflexion is noticeable in the curve relating the overvoltage and C.D. Some typical examples are incorporated in

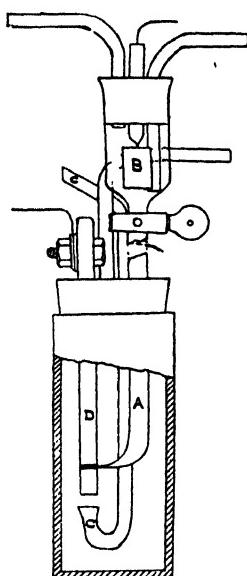


FIG. 1.

TABLE II.—OVERTOLERAGES OBTAINED BY DIRECT METHOD (MILLIVOLTS).

Solution.	Current Densities (Millamps./cm <sup>2</sup> ).							
	0.5.	1.0.	5.	10.	25.	50.	75.	300.
N . NaOH . . . .	—	75	385	440	480	600	800	—
Ca(OH) <sub>2</sub> (sat.) . . . .	300	450	550	650	715	900	—	—
Ca(OH) <sub>2</sub> (semi-sat.) . . . .	460	550	760	1050	1205	1450	—	—
Ba(OH) <sub>2</sub> (sat.) . . . .	50	340	425	425	435	455	460	600
N/37 NEt <sub>4</sub> OH . . . .	400	495	790	960	1170	1590	—	—
N/46 NMMe <sub>4</sub> OH . . . .	420	470	610	850	1075	—	—	—
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> (semi-sat.) . . . .	640	710	935	1100	1215	1505	1750	—
N . HNa <sub>2</sub> PO <sub>4</sub> . . . .	345	503	640	665	757	930	970	1750
N . Am <sub>2</sub> CO <sub>3</sub> . . . .	220	550	720	760	880	1120	—	2260

TABLE III.—OVERTOLERAGES OBTAINED BY COMMUTATOR METHOD (MILLIVOLTS).

Solution.	Critical C.D.	Current Densities (Millamps./cm <sup>2</sup> ).						
		0.3.	1.0.	5.	10.	25.	75.	500.
N . NaOH . . . .	10	22	350	430	460	460	460	460
Ca(OH) <sub>2</sub> (sat.) . . . .	10	150	350	445	460	460	460	—
Ca(OH) <sub>2</sub> (semi-sat.) . . . .	10	250	430	505	515	515	515	—
Ba(OH) <sub>2</sub> (sat.) . . . .	60	250	—	395	415	430	440	—
N/37 NEt <sub>4</sub> OH . . . .	10	280	495	535	545	545	545	—
N/46 NMMe <sub>4</sub> OH . . . .	1	300	470	460	460	460	460	—
N . Na <sub>2</sub> CO <sub>3</sub> . . . .	40	—	—	415	450	500	505	505
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> (semi-sat.) . . . .	3	240	675	700	700	700	700	700
N . HNa <sub>2</sub> PO <sub>4</sub> . . . .	50	230	490	550	560	610	675	675
N . Am <sub>2</sub> CO <sub>3</sub> . . . .	5	140	440	720	720	720	720	—
N . Na <sub>2</sub> SO <sub>4</sub> . . . .	30	300	615	—	745	773	775	775
N . KCl . . . .	70	—	—	780	—	875	895	895

Figs. 2 and 3; these also show some of the values in the neighbourhood of this point which have been omitted from Table II. The value of the overvoltage at this point is not far removed from the maximum constant value obtained by the commutator method.

(3) No apparent relation exists between the alkalinity of the electrolyte and the minimum C.D. for which a constant overvoltage is obtained.

Variation of Over-voltage with the Duration of the Interval of the Commutator. (Decay of Polarisation.)—Experiments were made with the interval commutator de-

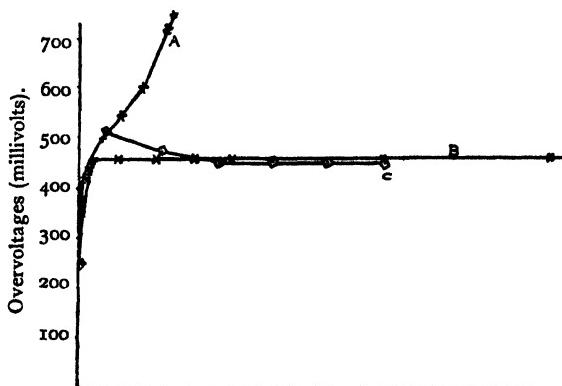


FIG. 2.—Overvoltages of N . NaOH.  
† Direct method (A). \* Commutator method (B).  
Decay curve (C).

scribed previously. The latter consists essentially of 64 metallic segments fitted on an insulated revolving core. Any one or all of these could be connected with metal slip ring on either side by means of small screws in communication with the latter. The brush making contact on the revolving segments was connected to the working electrode, and it was thus possible to connect the latter during time-intervals equal to that of  $1/64$  of a revolution to either the source of current or to the potentiometer. Thus, if 32 successive segments were connected to the current slip-ring, 32 being left unconnected and if, further, these latter were connected individually in

successive experiments to the potentiometer slip-ring C and the number of revolutions of the commutator was  $r$  per min., the current would pass through the cathode during  $32/64 \cdot r$  min. and would be off for an equal time, during which the average cathode potential could be measured in intervals of  $1/64 \cdot r$  min.

The main difficulty was due to electrical leakage, but this was over-

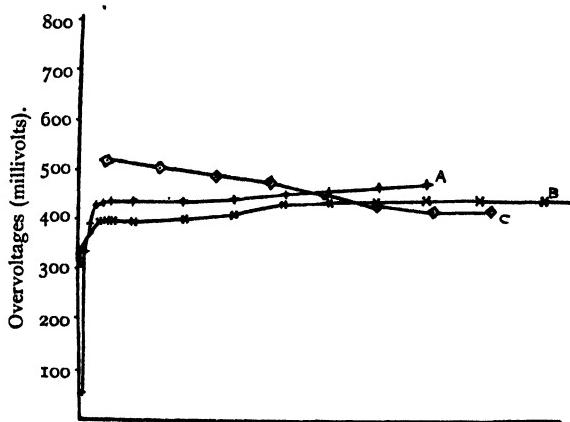


FIG. 3.—Overvoltages of saturated  $\text{Ba}(\text{OH})_2$ .

† Direct method (A). \* Commutator method (B).  
° Decay Curve (C).

come by placing the apparatus on insulating material resting on earthed metal plates, and by brushing out any metal or dust from between the segments after each experiment. Further a blank segment was left at the beginning and end of each series of segments connected to the current slip-ring in order further to obviate leakages. In no cases were leaks detectable when these precautions were taken.

The speed at which the instrument was run in most of the experiments recorded was 4200 revs. per min. Some of the results are shown in Table IV. The C.D. used had either the critical or a higher value in all cases except that of baryta in which case it was 40 milliamps./cm.<sup>2</sup>

TABLE IV.

Solution.	Intervals after Interrupting the Current ( $10^{-4}$ secs.).										
	1'.	3'.	5'.	7'.	9'.	12'.	14'.	16'.	18'.	20'.	29'.
$\text{N} \cdot \text{NaOH}$	518	475	450	455	455	455	—	—	—	—	—
$\text{Ba}(\text{OH})_2$ (sat.)	515	500	485	475	460	435	420	420	—	—	—
$\text{N} \cdot \text{Na}_2\text{CO}_3$	650	600	530	450	450	445	440	445	—	—	—
$\text{Na}_2\text{B}_4\text{O}_7$ (semi-sat.)	790	785	745	730	720	715	717	705	695	705	705
$\text{N} \cdot \text{HNa}_2\text{PO}_4$	680	615	605	600	600	602	—	—	—	—	—
$\text{N} \cdot \text{Na}_2\text{SO}_4$	825	795	770	755	760	760	—	—	—	—	—
$\text{N} \cdot \text{KCl}$	1020	980	970	965	950	940	935	930	915	910	910

The readings are the mean values of the overvoltages (in millivolts) during the intervals concerned. The intervals stated thus represent the

times between the breaking of the current and the reading of the overvoltage reckoned from the centre of the segment concerned. It will be noted that the overvoltages drop rapidly from high values to constant values which, as a rule, are not far removed from those obtained by the "direct" and "commutator" methods. In general they were analogous to those recorded for antimony, the overvoltages being read at times and C.D. above the critical values shown in Tables I. and III., respectively. Preliminary experiments showed that the general conclusions drawn from the results already referred to held whatever the time interval. In Figs. 2 and 3 the three sets of results are compared for certain of the electrolytes, (*N.* NaOH and saturated Ba(OH)<sub>2</sub> respectively).

*Variation of the Overvoltage with the Hydrogen Ion Concentration of the Electrolyte.*—The " $\rho_H$  voltage," or the voltage between a saturated calomel electrode and a hydrogen electrode placed in the solution, was determined for each electrolyte investigated. Table V. summarises the results obtained, the columns A, B, and C showing the values of the overpotentials obtained (in millivolts) by the direct, commutator and decay-curve methods, respectively.

TABLE V.—SUMMARY OF OVERPOTENTIALS.

Solution.	$\rho_H$ Voltage (Millivolts).	Direct. A.	Comm. B.	Decay. C.
<i>N.</i> NaOH . . .	1060	450	460	455
Ca(OH) <sub>2</sub> (sat.) . .	1010	465	460	—
Ca(OH) <sub>2</sub> (semi-sat.) . .	970	545	515	—
Ba(OH) <sub>2</sub> (sat.) . .	1005	440	440	450
<i>N</i> /37. <i>N</i> . H <sub>4</sub> OH . .	920	545	545	—
<i>N</i> /46. <i>N</i> . Me <sub>4</sub> OH . .	915	455	460	—
<i>N</i> . Na <sub>2</sub> CO <sub>3</sub> . . .	910	—	500	445
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> (semi-sat.) . .	785	715	700	700
<i>N</i> . HNa <sub>2</sub> PO <sub>4</sub> . . .	780	675	675	600
<i>N</i> . Am <sub>2</sub> CO <sub>3</sub> . . .	760	730	720	—
<i>N</i> /2Am <sub>2</sub> CO <sub>3</sub> . . .	760	—	720	—
<i>N</i> . Na <sub>2</sub> SO <sub>4</sub> . . .	655	—	775	760
<i>N</i> . KCl . . .	655	—	895	910

In the graph shown in Fig. 4, the abscissæ represent the  $\rho_H$  voltages, and the ordinates the corresponding overvoltages as determined by the three methods. The numbers attached are for the purposes of identification with the results shown in Table V., *N.* NaOH being No. 1 and *N.* KCl No. 13.

It will be seen that the graph obtained is in the neighbourhood of a straight line corresponding with the relationship,  $w + h = \text{constant}$  (1.5). It is not intended at present to do more than indicate the possibility of the existence of any such relationship, since the effects of secondary interfering influences have yet to be more fully investigated. At the same time it should be pointed out that the results given above are reproducible under the conditions of the experiments stated, and that the recorded variations from the straight line are considerably in excess of the experimental error, which is in the neighbourhood of 7 to 10 millivolts.

As regards the values for neutral solutions it should be pointed out that in these cases it is difficult to obtain readings owing to the rapidity with which the  $\rho_H$  value in the neighbourhood of the electrodes is changing during electrolysis. Further, it will be noted, the values of the overvoltage determined by the three different methods are usually in agreement, aberra-

tions from the straight line relation being due to the peculiarities of the individual electrolytes.

In this connection the buffering capacities of each of the solutions was determined in terms of the number of millimols of sodium hydroxide required to produce a change in the  $\rho_H$  voltage of 20 millivolts when titrated electrometrically into one litre of the solution. The results obtained however, by no means fully explained the variations. Moreover, the production

of high results in the presence of a deposit on the cathode owing to a condenser effect also fails to explain the results completely. Again, cathodic action may result in the production of colloidal solutions, silver being in fact found in solution in every case. The addition, however, of a colloidal solution of silica produced no alteration in overvoltage. As a result of these influences acting in opposite senses, the fact that a certain amount of compensation may occur in some cases must not be overlooked. It is intended to discuss this problem more fully in a future paper when the results of further experiments can be included.

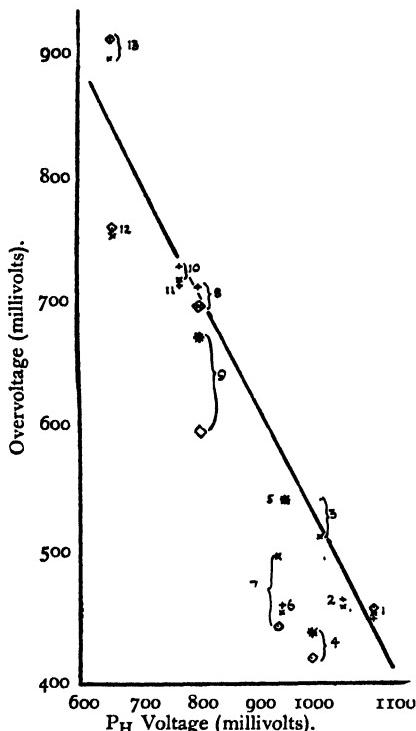


FIG. 4.—Relationship between  $\rho_H$  Voltage and Overvoltage.

- † Direct Method (A).
- Commutator Method (B).
- Decay Curve (C).

3. The overvoltage as measured by the direct method increases rapidly with the C.D. and the overvoltage—C.D. curves show a point of inflexion, or change of direction at a certain point.

4. This point is close to the values of the overvoltages obtained by the "commutator" method.

5. The overvoltages obtained by the commutator method increase rapidly with the C.D. up to a point, beyond which they remain constant.

6. The decay-curves of polarisation sink to a value which remains nearly constant over a considerable time and which usually approximates to those obtained by the above methods.

7. A linear connection between the  $\rho_H$  voltage and the overvoltage of the solution is indicated graphically. The deviations may possibly be due to secondary influences yet to be investigated.

Considerations based on the buffer actions of the various solutions and

### Conclusions.

1. The overpotential, as defined in the introduction, of a silver cathode in a number of neutral and alkaline solutions has been investigated.

2. The overvoltage increases rapidly with the duration of the electrolysis up to a certain point, when it remains constant. The time taken to arrive at this point decreases as the electrolytes approach the neutral-point.

3. The overvoltage as measured by the direct method increases rapidly with the C.D. and the overvoltage—C.D. curves show a point of inflexion, or change of direction at a certain point.

4. This point is close to the values of the overvoltages obtained by the "commutator" method.

5. The overvoltages obtained by the commutator method increase rapidly with the C.D. up to a point, beyond which they remain constant.

6. The decay-curves of polarisation sink to a value which remains nearly constant over a considerable time and which usually approximates to those obtained by the above methods.

7. A linear connection between the  $\rho_H$  voltage and the overvoltage of the solution is indicated graphically. The deviations may possibly be due to secondary influences yet to be investigated.

Considerations based on the buffer actions of the various solutions and

on the effect of an insoluble layer on the electrode fail to account completely for the deviations, but the possibility of compensating influences cannot be ignored.

8. The conditions of the formation of a black deposit on the silver, and the effect of this on the overvoltages have been investigated.

9. In general the results are analogous to those already obtained for an antimony cathode in neutral and alkaline solutions.<sup>1</sup>

In conclusion the author wishes to express his indebtedness to Dr. H. J. S. Sand, F.I.C., under whose supervision the above work was carried out.

*Sir John Cass Technical Institute,  
E.C. 3.*

### JOINT DISCUSSION

On papers by Messrs. BYRNE,<sup>1</sup> SMITH,<sup>2</sup> GRANT,<sup>3</sup> and BOWDEN<sup>4</sup>

**The President** called attention to that part of the paper by Mr. Smith which described the use of radio parts in the building up of electrolytic apparatus. He had himself found that such parts could often be substituted for more expensive rheostats, etc., and that the whole apparatus could be assembled cheaply and conveniently.

Referring to Dr. Rideal's remarks in presenting Mr. Bowden's paper, he would point out that silver was a metal which could form compounds with platinum. It would be interesting to repeat the experiment with gold, which did not form compounds but entered into solid solution, and with some other metal which was completely insoluble in the solid state. One would expect that the potential developed when a single layer of metallic atoms was deposited on a cathode of another metal would vary according as there existed a certain chemical affinity between the two metals or not. The rate of change of potential with the thickness of the deposited layer should also be different in the two cases.

**Dr. E. K. Rideal** said that the problem of hydrogen overpotential appeared to involve similar problems to that found in the deposition of metals in thin films. If a metal A be coated with a metal B in a solution containing ions of B they must enquire into the fundamental point how the potential of the electrode varied as the deposit got thicker. It was, of course, well known that when a few molecular layers had been deposited, the electrode behaved as one consisting of the metal B. He saw no reason for the assumption which is always made that as the first layer is being formed the potential will be determined by a Nernst relationship  $V = \frac{RT}{F} \ln \frac{X \cdot C_M}{f_M C_M}$ , where  $C_M$  is the surface concentration of the metal in the solution of ionic activity  $f_M C_M$ . It was much more probable that V and  $C_M$  would be directly related. We may likewise anticipate that the free energy of the atoms of B on A will differ from those of B on its own substrate, and thus as the layers thicken the potential should vary until we obtain that characteristic of the metal.

**Mr. J. Grant** asked whether there was any difficulty experienced in cleaning the apparatus pictured in Fig. 3 of Mr. Smith's paper, on account of the dead-space between R and S?

**Dr. H. J. S. Sand** (*communicated*), said that he had been interested in Mr. Byrne's paper. He, however, wished to point out that the measure-

<sup>1</sup> Vol. 23, p. 660.

<sup>2</sup> See p. 216 *ante.*

<sup>3</sup> See p. 225 *ante.*

<sup>4</sup> Vol. 23, p. 571.

ment of electrode resistance during the passage of a current for the purpose of estimating true polarisation, was not new. In 1904 he (Dr. Sand) had fully described a method of this kind.<sup>1</sup>

Essential differences between the two methods were:—

1. That his (Dr. Sand's) apparatus was arranged for horizontal electrodes forming the ends of long straight tubes, so that convection currents should be eliminated and a uniform current density be obtained.

2. That a connection was tapped off to auxiliary electrodes 3 to 4 mm. from the electrode under examination; thus the potential of one electrode only and the resistance of a column of electrolyte of only 3 to 4 mm. were measured; no chokes were required. For further details which differed in many respects from those given by Mr. Byrne, reference must be made to the original paper. It might be pointed out, that in this paper (p. 12) it was shown, probably for the first time, that at electrodes generally considered reversible also, *viz.*, at copper in copper sulphate, an additional voltage (overvoltage) of about 20 millivolts was observed during the passage of the current, which was definitely proved not to be referable to changes of concentration of the electrolyte.

**Mr. Byrne** (*communicated*) said that Dr. Sand used a totally different method to that described. He used an auxiliary standard electrode to measure the potential of one electrode and eliminated the ohmic potential drop in the solution by comparing the resistances between a second auxiliary electrode (platinum) and the anode and cathode. These were compared by a type of capacity bridge. The standard bridge resistances had to carry all the electrolysing current which was consequently varied during the measurement; furthermore, the current, potential, and resistance could not be measured simultaneously. It was assumed that one electrode remained non-polarisable and constant and that the resistance between the platinum auxiliary electrode and (*e.g.*) the cathode was the same as that between the standard and the latter. These assumptions limited the method to currents of at most a few milli-ampères. The use of chokes was avoided by putting the battery in shunt with the whole bridge: a method which is not altogether desirable. It might be mentioned that Scott also described a method of putting a cell in an A.C. bridge.<sup>2</sup> He put the battery in series with the detector and used the bridge for measuring "polarisation capacity."

**Mr. Bowden** in reply to the President's remarks said that during the deposition of the first atomic layer of silver on a platinum cathode in silver nitrate solution the potential rose to a value 100 millivolts more negative than the silver electrode and on further deposition fell gradually to the potential characteristic of massive silver. That is, the "solution pressure" of silver atoms was greater on a platinum surface than on a silver one, indicating that if a Pt/Ag compound were formed under these conditions, its free energy was greater than that of massive silver. The behaviour of different types of compound was certainly of interest; *cf.* for example, the deposition of iron atoms on a mercury surface where it was well known that the solution pressure of the amalgam was greater than that of massive iron. It was proposed to study these shortly. The investigation was not quite a simple one since other ions present in the electrolyte (*e.g.* hydrogen) could deposit with the metal and affect the potential. Up to the present the work had been confined mainly to the study of hydrogen. It was found that the deposition of  $6 \times 10^{-2}$  qm. ions of hydrogen per true square centimeter on a metallic cathode raised the potential 100 millivolts. The relation between the amount of hydrogen added to the plate and the

<sup>1</sup> *Trans. Faraday Soc.*, 1, 1 (1904).

<sup>2</sup> *Ann. Physik.*, 1899, 67, 388.

over-potential was a linear one over a wide range of potential. This quantity  $6 \times 10^{-12}$  qm. ions/cm.<sup>2</sup> was very small indeed, being sufficient only to form  $1/3000$  of an atomic layer. It varied only with the true area of the cathode surface and was independent of the nature of the underlying metal.

**Mr. Smith** said that when emptying and washing the electrode vessel (Fig. 3 pattern) it was desirable that the stopper at M which bore the platinum electrode should be removed. This enabled the liquid contained in the bulb Q to be emptied and the dead space could then without any difficulty be flushed out with water *via* the comparatively wide tube MP. If the taps H and L were both open all the tubes would be washed out by water entering at M.

## PERPHOSPHORIC ACIDS AND PERPHOSPHATES.

By SYED HUSAIN AND J. R. PARTINGTON.

*Received 28th October, 1927.*

### Historical.

Electrolysis of orthophosphoric acid does not give rise to perphosphoric acids,<sup>1, 2, 3</sup> even in presence of hydrofluoric acid.<sup>4</sup> In presence of hydrogen peroxide, however, a small quantity of permonophosphoric acid is produced.<sup>3</sup>

By the action of 30 per cent. or stronger hydrogen peroxide on phosphorus pentoxide, meta- or pyro-phosphoric acid, permonophosphoric acid,  $H_3PO_5$  is produced; in the presence of an excess of pyrophosphoric acid a perphosphoric,  $H_4P_2O_8$  is also formed. The two acids resemble the corresponding persulphuric acids in their properties; the permonophosphoric acid is, however, a stronger oxidising agent than the Caro's acid.<sup>3</sup>

Siebold<sup>5</sup> claims to have prepared "perphosphoric acid" by the action of 31 per cent. hydrogen peroxide on phosphorus oxychloride and a "true sodium perphosphate" by neutralising the "perphosphoric acid" with alcoholic sodium hydroxide. This statement is now found to be incorrect.

Sodium phosphate cannot be oxidised electrolytically,<sup>4</sup> but several phosphates of sodium containing active oxygen have been prepared by the action of hydrogen peroxide. They are described as perphosphates in patent literature, but are really compounds of hydrogen peroxide. The  $NaPO_4$  of Alvarez<sup>6</sup> is an indefinite mixture of sodium phosphate and sodium peroxide.<sup>7</sup> Aschkenasi and Rudenko have prepared several compounds containing active oxygen by dissolving the phosphate in hydrogen peroxide and afterwards (according to Aschkenasi) evaporating the solution at a mild temperature and a reduced pressure, or (according to Rudenko) precipitating the solution with alcohol or evaporating it on a water-bath. Thus the following compounds are described (see next page).

True potassium perphosphates were prepared in solution by electrolysing a concentrated solution of secondary potassium phosphate containing fluoride and a small quantity of chromate, between platinum electrodes at a low temperature with a low anodic current density.<sup>4</sup> Cautious evaporation of the electrolysed solution gave solid potassium perphosphate,  $K_4P_2O_8$ .<sup>8</sup>

<sup>1</sup> Hittorf, *Pogg. Ann.*, 1853, **89**, 209.

<sup>2</sup> Lucknow, *Z. anal. Chem.*, 1880, **19**, 1.

<sup>3</sup> Schmidlin and Massini, *Ber.*, 1910, **43**, 1162.

<sup>4</sup> Fichter and Müller, *Helv. Chim. Acta*, 1918, **1**, 304.

<sup>5</sup> D.R.P., 279,306.

<sup>6</sup> *Chem. News*, 1906, **94**, 269.

<sup>7</sup> Rudenko, *J. Russ. Physical Chem. Soc.*, 1912, **44**, 1215.

<sup>8</sup> Fichter and Rius Y. Miro, *Helv. Chim. Acta*, 1919, **2**, 3.

Phosphate of Sodium.	Concentration of Active Oxygen (Per Cent.).	Author.
Primary ortho-	2	Aschkenasi, <i>D.R.P.</i> , 299300, 296796
Secondary "	10 ( $\text{Na}_2\text{HPO}_4 \cdot \text{H}_2\text{O}_2$ )	Rudenko, <i>loc. cit.</i> , 1209
" "	2·8 ( $\text{Na}_2\text{HPO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}_2 \cdot 6\text{H}_2\text{O}$ )	{ Chem. Werke vorm. H. Byk, <i>D.R.P.</i> , 287588
" "	8·9	Aschkenasi, <i>D.R.P.</i> , 299300
" "	1·4 and 7	" <i>D.R.P.</i> , 316997
" "	12	" <i>D.R.P.</i> , 318219
" "	8·8	Petrenko, <i>J. Russ. Physic. Chem. Soc.</i> , 1902, 34, 204; Rudenko, <i>loc. cit.</i> , 1209
Tertiary "	8·95 ( $\text{Na}_3\text{PO}_4 \cdot 2\text{H}_2\text{O}_2 \cdot 4\frac{1}{2}\text{H}_2\text{O}$ )	Aschkenasi, <i>D.R.P.</i> , 299300
" "	1·4 and 2·8	" <i>D.R.P.</i> , 316997
Pyro-	13·7	Rudenko, <i>loc. cit.</i> , 1214
" "	10·65 ( $\text{Na}_4\text{P}_2\text{O}_7 \cdot 2\frac{1}{2}\text{H}_2\text{O}_2$ )	Chem. Werke vorm. H. Byk, <i>loc. cit.</i>
" "	8·5	<i>Ges. f. chem. Industrie</i> , <i>D.R.P.</i> , 293786
Meta	12·75 ( $\text{Na}_4\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}_2$ )	Rudenko, <i>loc. cit.</i> , 1212
	3	

A secondary potassium phosphate containing 7·1 per cent. of active oxygen was obtained by the action of hydrogen peroxide.<sup>9</sup> In a manner analogous to potassium perphosphates, rubidium and ammonium perphosphates were prepared in solution by electrolysis.<sup>4</sup> By the action of hydrogen peroxide a secondary ammonium phosphate containing 5·6 per cent. of active oxygen,<sup>7</sup> and a tertiary ammonium phosphate containing 12·65 per cent. of active oxygen<sup>10</sup> were obtained. Primary barium phosphate containing 1·5 per cent. of active oxygen was prepared by dissolving barium peroxide in phosphoric acid or by the action of hydrogen peroxide on primary barium phosphate.<sup>11</sup>

The literature of the subject is incomplete and true perphosphates have not been distinguished from phosphates with hydrogen peroxide of crystallisation. The subject, therefore, seemed to merit further investigation.

#### Criteria for True Perphosphates.

As a result of the present work it was found that true perphosphates do not give any of the characteristic reactions of hydrogen peroxide with permanganic acid, chromic acid and ether, or titanic acid (as do the phosphates containing hydrogen peroxide of crystallisation). On the other hand, they oxidise acidified manganous salt solutions to permanganic acid, acidified aniline solution to nitrosobenzene, which is then slowly oxidised to nitrobenzene, and silver nitrate solution to a black precipitate, which gradually turns yellow. Ammonium perphosphates, however, do not give the last-mentioned reaction (analogy with ammonium persulphate). It is interesting to note that perphosphoric acids are obtained only by the action of hydrogen peroxide; while the action of the same reagent on phosphates gives rise to pseudo-perphosphates. True perphosphates are obtained only by electrolysis.

#### Experimental.

The experimental work was divided into two parts: (a) the action of hydrogen peroxide on phosphates; (b) electrolytic oxidation of phosphates. Great care was taken to ensure the purity of all materials used.

<sup>9</sup> Chem. Werke vorm. H. Byk, *D.R.P.*, 287,588.

<sup>10</sup> Petrenko, *J. Russ. Phys. Chem. Soc.*, 1902, 34, 204.

<sup>11</sup> Aschkenasi, *D.R.P.*, 296,796.

TABLE I.

Phosphate.	Solu- bility <sup>†</sup> in $H_2O_2$ and Reaction.	Analysis of the Dry Product (Per Cent.).						Probable Formula of Product.	Remarks.
		Active Oxygen. Determined.	PO <sub>4</sub> . Calculated.	R. <sup>*</sup> Determined.	PO <sub>4</sub> . Calculated.	R. <sup>*</sup> Calculated.	Loss on Heating to 50° C. in vacuo.		
$LiH_2PO_4$	S. A.	0·06	—	—	—	—	—	$Li_3PO_4 \cdot 0\cdot25 H_2O$	Completely decomposes in a month.
$Li_3PO_4 \cdot 0\cdot5 H_2O$	I. B.	3·67	3·73	—	—	—	—	$Li_3PO_4 \cdot 0\cdot25 H_2O$	Loses 4·4 per cent. of active oxygen in 3 days.
$Li_4P_2O_7 \cdot 2 H_2O$	I. B.	0·84	1·96	—	—	—	—	$Li_4P_2O_7 \cdot 0\cdot25 H_2O$	Very stable, no loss of active oxygen in a week.
$KH_2PO_4$	S. A.	11·28	11·19	—	—	—	—	$KH_2PO_4 \cdot r\cdot25 H_2O$	Violent reaction with rapid decomposi-
$K_2HPO_4$	S. B.	15·75	15·43	36·25	36·05	—	—	$K_2HPO_4 \cdot 2\cdot5 H_2O$	tion of $H_2O_2$ .
$K_3PO_4$	S. B.	nil	—	—	—	—	—	—	Loses 0·6 per cent. of active oxygen in a fortnight.
$K_4P_3O_7 \cdot 3 H_2O$	S. B.	12·24	11·11	31·52	32·83	$P_2O_5$	—	$K_4P_3O_7 \cdot 3 H_2O$	Loses 0·47 per cent. of active oxygen in a week. Loss on heating corresponds to loss of $r\cdot5 H_2O_2 + O_2$ .
$Rb_2HPO_4 \cdot H_2O$	S. B.	11·61	11·36	26·90	27·00	—	—	$Rb_2HPO_4 \cdot 2\cdot5 H_2O$	Loses 0·81 per cent. of active oxygen in 3·5 weeks. Loss on heating corresponds to loss of $0\cdot5 H_2O_2 + O_2$ .
$Cs_2HPO_4 \cdot H_2O$	S. B.	6·20	5·82	22·75	23·03	—	—	$Cs_2HPO_4 \cdot r\cdot5 H_2O$	—
$NH_4H_2PO_4$	S. A.	0·275	—	—	—	—	—	$(NH_4)_2HPO_4 \cdot 0\cdot75 H_2O$	Completely decomposes in a month.
$NaNH_4HPO_4 \cdot 4H_2O$	S. B.	6·73	7·61	—	—	—	—	$NaNH_4HPO_4 \cdot 0\cdot75 H_2O$	Loses 1·77 per cent. of active oxygen in 2 months.
$(NH_4)_2H_4P_2O_7$	S. A.	7·01	7·38	58·99	58·45	—	—	$(NH_4)_2H_2P_2O_7 \cdot H_2O_2 \cdot 2H_2O$	Loses 1·84 per cent. of active oxygen in 11 days.
$CaH(PO_4)_2$	S. A.	none	—	—	—	—	—	$CaHPO_4 \cdot 0\cdot5 H_2O$	—
$CaHPO_4$	I. A.	5·5	5·23	—	—	—	—	—	Loses 3·14 per cent. of active oxygen in a month.
$SrH(PO_4)_2$	S. A.	none	—	—	—	—	—	$SrHPO_4 \cdot r\cdot5 H_2O$	—
$SrHPO_4$	I. A.	9·88	10·21	—	—	—	—	$BaHPO_4 \cdot r\cdot5 H_2O$	Loses 6·26 per cent. of active oxygen in a fortnight.
$BaHPO_4$	I. A.	8·40	8·45	33·41	33·45	—	—	—	Loses 3·18 per cent. of active oxygen in a fortnight.
$TlH_2PO_4$ or $Tl_2HPO_4 \cdot 2 H_2PO_4$	I. A.	none	—	—	—	—	—	—	Special methods were devised to estimate the active oxygen.
	I. N.	0·2	—	—	—	—	—	—	—

\* R represents the metal, for example, Na, K, etc.

<sup>†</sup> S.—Soluble. I.—Insoluble. A.—Acid. B.—Alkaline. N.—Neutral.

(a) Calculated, 48·55 per cent. (b) Calculated, 64·36 per cent. (c) Calculated, 48·24 per cent. (d) Calculated, 19·04 per cent. (e) Calculated, 8·0 per cent.

*1. The Action of Hydrogen Peroxide on Phosphorus Compounds.*

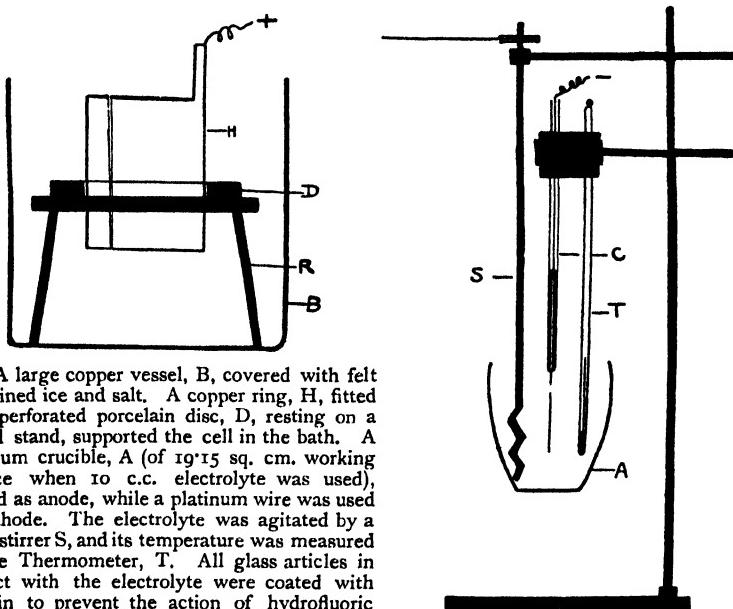
*Phosphorus Oxychloride.*—Siebold's<sup>5</sup> work was repeated, but his results could not be confirmed. The action of 30 per cent. hydrogen peroxide on phosphorus oxychloride at 0° in quantities expressed by the equation,



gives rise only to a mixture of phosphoric acid and free hydrogen peroxide. Much chlorine is evolved during the reaction, owing to the oxidation of the resulting hydrochloric acid by hydrogen peroxide.<sup>12</sup> When the mixture so obtained is neutralised with alcoholic sodium hydroxide, a white precipitate is produced, which gives the reactions of free hydrogen peroxide and is, therefore, not a true perphosphate.

*Phosphates.*—The action of hydrogen peroxide was investigated on

FIG. I.



A large copper vessel, B, covered with felt contained ice and salt. A copper ring, H, fitted in a perforated porcelain disc, D, resting on a tripod stand, supported the cell in the bath. A platinum crucible, A (of 10·75 sq. cm. working surface when 10 c.c. electrolyte was used), served as anode, while a platinum wire was used as cathode. The electrolyte was agitated by a glass stirrer S, and its temperature was measured on the Thermometer, T. All glass articles in contact with the electrolyte were coated with paraffin to prevent the action of hydrofluoric acid. A milli-ammeter and a copper coulometer were included in the circuit. A voltmeter measured the difference of potential across the cell.

several phosphates. The phosphate in question was dissolved or suspended in 30 per cent. hydrogen peroxide, and the resulting mixture was evaporated to dryness at room temperature in a vacuum (about 5 mm. press.) over fused calcium chloride. The same results were obtained in the case of ammonium compounds when instead of calcium chloride sodium hydroxide was used as a drying agent.

The results are summarised in the table on p. 237.

It was found that agar agar or waterglass do not improve the stability of  $\text{K}_4\text{P}_2\text{O}_7$ ,  $3\text{H}_2\text{O}_2$  or of  $\text{NaNH}_4\text{HPO}_4 \cdot 0\cdot75\text{H}_2\text{O}_2$ .

*Properties.*—All these substances in the dry state evolve hydrogen peroxide on warming, and liberate iodine slowly from a neutral 30 per cent.

<sup>12</sup> See Aloy, etc., and Moissan, *Traité de Chimie minérale*, vol. I., p. 271.

potassium iodide solution. In aqueous solution they decolorise permanganic acid, produce a blue coloration with chromic acid and ether and a yellow coloration with titanic acid. With silver nitrate solution they give a yellow precipitate or a white one if they are prepared from a pyrophosphate.

## 2. Electrolytic Oxidation.

*Apparatus.*—The apparatus used for electrolysis is shown in Fig. 1.

*Method of Electrolysis.*—Usually 10 c.c. of solution were placed in the crucible and electrolysed at about 0° C. with an anodic current density of nearly 0·146 amp./cm.<sup>2</sup> for 3 to 5 hours. At the end of electrolysis the copper deposited in the coulometer was weighed. The electrolysed solution was diluted to 100 c.c., 10 c.c. of which were analysed each time by adding to 200 c.c. of acidified potassium iodide solution (2 g. of KI, 100 c.c. of H<sub>2</sub>O and 15 c.c. of H<sub>2</sub>SO<sub>4</sub> (1 : 2)). The iodine liberated *immediately* and that *after a day* were titrated with 0·1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution with freshly prepared starch solution as indicator. Blank titrations were always made to check the results. The iodine-value of the chromate present was subtracted from the amount of iodine liberated immediately.

## Special Experiments.

### Lithium.

Lithium did not give satisfactory results. The only soluble phosphate of lithium, LiH<sub>2</sub>PO<sub>4</sub> was electrolysed under different conditions, for example (a) with a little chromate and acid lithium fluoride (normal fluoride is insoluble) or without any fluoride, (b) with a porcelain diaphragm, and (c) with superimposition of an alternating current of high frequency (from an induction coil) on a direct current and a diaphragm. In all these experiments a precipitate consisting of tertiary lithium phosphate and lithium fluoride or of the former only immediately appeared at the cathode. The resistance of the cell increased with the increase in the amount of the precipitate, with the result that the current ceased to flow and the temperature went up.

### Sodium.

On account of its greater solubility (3·16 per cent.) than that of secondary sodium phosphate (about 1·67 per cent.) which had failed to give rise to perphosphates by electrolysis,<sup>4</sup> sodium pyrophosphate was electrolysed. A saturated solution of sodium pyrophosphate containing 1*M* sodium fluoride and 0·0035 g. of potassium chromate per 10 c.c. was electrolysed for 5 hours. The electrolysed solution was found to contain no active oxygen.

### Rubidium and Caesium

Electrolysis of concentrated solutions of secondary rubidium phosphate, Rb<sub>2</sub>HPO<sub>4</sub> · H<sub>2</sub>O or secondary caesium phosphate, Cs<sub>2</sub>HPO<sub>4</sub> · H<sub>2</sub>O, in the presence of about 0·35 g. of chromate and even without the addition of fluoride gives rise to perphosphates, if a low anodic current density (nearly 0·146 amp./cm.<sup>2</sup>) is used.

*Properties.*—The freshly electrolysed solutions do not show any of the characteristic reactions of hydrogen peroxide with permanganic acid, chromic acid and ether or titanic acid. On the other hand, acidified manganous salt solutions give an intense pink coloration of permanganic acid immediately on warming or after half an hour in the cold. Aniline solution, acidified with dilute sulphuric acid, gives a green solution on

TABLE II.

Electrolyte.	$C.c \frac{N}{10} \times Na_2S_2O_3 - Soln.$ in 1 Amp. Hr.		Current Efficiency in Percentage.		
	Immediately.	After 18 Hrs.	$H_3PO_6$ .	$H_4P_2O_8$ .	Total.
10 c.c. of 2·91 M $Rb_3HPO_4 \cdot H_2O + 0\cdot0035$ g. of $K_2CrO_4$	65·01	45·93	17·43	12·32	29·75
5 c.c. of 2·88 M $Cs_3HPO_4 \cdot H_2O + 0\cdot0017$ g. of $K_2CrO_4$	32·35	41·75	17·30	22·33	39·63

warming, which gradually turns brown. Silver nitrate solution gives a black precipitate, which slowly turns yellow. Ferrous sulphate solution is oxidised in the cold. Manganous sulphate solution gives a brown precipitate, which dissolves to a pink solution in dilute sulphuric acid. Solutions of salts of cobalt and nickel give precipitates with evolution of ozonised oxygen. Iodine is liberated immediately from a neutral 30 per cent. potassium iodide solution.

Rubidium and caesium permonophosphate are very unstable and continuously evolve oxygen from the time of their formation, decomposing completely in about 8 hours. But the corresponding perphosphates are fairly stable. The freshly electrolysed solutions, after keeping for 24 hours, contained the same amount of perphosphate and showed all the reactions of the freshly electrolysed solutions, except that they did not liberate iodine immediately from a neutral or an acidified solution of potassium iodide.

By allowing electrolysed solutions to evaporate at ordinary temperature in a vacuum over concentrated sulphuric acid, solid products containing rubidium and caesium perphosphates were obtained, in an impure condition, which gave the same reactions as those shown by the solutions which had been kept for 24 hours. On account of their extreme solubility the rubidium and caesium perphosphates, however, could not be prepared in the pure condition.

#### Ammonium.

The influence of various factors that govern the electrolytic oxidation of ammonium phosphates was thoroughly investigated with the object of increasing the current efficiency and ultimately isolating the solid ammonium perphosphate. Secondary ammonium phosphate was used throughout.

(i) The current efficiency gradually decreased with increase of anodic current density except in the case of experiment No. 6 (Table III.).

(ii) The current efficiency decreased and the total content of perphosphates increased with increasing duration of electrolysis except in the case of experiment No. 1 (Table IV.).

(iii) The current efficiency decreased with the rise of temperature (Table V.).

(iv) The current efficiency of perphosphate increased with increasing concentration of the phosphate, while that of permonophosphate increased to a maximum and then fell (Table VI.).

(v) Using 3 M secondary ammonium phosphate the current efficiency of perphosphate (Table VII.) rapidly increased with increasing concentration of ammonium fluoride, until it reached a maximum somewhere between 2 and 3 M, and then began to decrease gradually. The current efficiency of permonophosphate reached the maximum at about 4 M

ammonium fluoride and then became almost constant. The total current efficiency was highest at about 3 M ammonium fluoride.

(vi) Using 4 M secondary ammonium phosphate (Table VIII.) the current efficiency of perphosphate was again highest at 3 M ammonium fluoride, while the current efficiency of permonophosphate and the total current efficiency gradually increased with the concentration of fluoride. The maximum yield of perphosphate obtained was higher than that in Table VII.

(vii) The current efficiency of perphosphate and the total current efficiency were highest at a concentration corresponding to 0.32 g. of ammonium chromate per lit., while the current efficiency of permono-phosphate gradually increased with the concentration of the chromate. (See Table IX.).

TABLE III.—THE INFLUENCE OF ANODIC CURRENT DENSITY.

For small C.D. the platinum crucible, A, Fig. 1, served as anode; for higher C.D. a piece of platinum foil of 1 sq. inch area was used. Variations in C.D. were effected by diminishing the surface of the anode by covering it with a layer of marine glue.

The electrolyte contained 1 M secondary ammonium phosphate, 1.2 M ammonium fluoride and 0.32 g. of ammonium chromate (added as ammonium dichromate) per litre. 10 c.c. of this solution were electrolysed each time at about +5° C. for an hour. The current intensity was varied between 0.21 and 0.33 amp.

Anodic Current Density in Amp./cm. <sup>2</sup> .	Coulometer g. Cu.	C.c. $\frac{N}{10} \times \text{Na}_2\text{S}_2\text{O}_3$ - Soln.		Current Efficiency (Per Cent.).		
		Immediately.	On the Following Day.	$\text{H}_3\text{PO}_5$	$\text{H}_4\text{P}_2\text{O}_8$	Total
0.01097*	0.3959	14.71	7.34	11.93	5.96	17.89
0.0149	0.4002	12.88	8.76	7.03	7.03	17.37
0.0184	0.3868	11.10	7.98	9.22	6.63	15.85
0.0263	0.4002	10.72	7.98	8.60	6.41	15.01
0.0368	0.3781	5.63	4.76	4.78	4.05	8.83
0.0682	0.3792	8.27	4.76	7.01	4.04	11.05
0.7813	0.3645	4.21	3.15	3.71	2.78	6.49
Pt wire	0.3463	3.25	3.09	3.01	2.87	5.88

TABLE IV.—THE INFLUENCE OF DURATION OF ELECTROLYSIS.

Conditions as in Table III., the anodic C.D. being 0.01671 amp./cm.<sup>2</sup>, but the time was varied.

Time in Min.	Coulometer g. Cu.	C.c. $\frac{N}{10} \times \text{Na}_2\text{S}_2\text{O}_3$ - Soln.		Current Efficiency. (Per Cent.).			Content. G./Lit.		
		Immediately.	On the Following Day.	$\text{H}_3\text{PO}_5$	$\text{H}_4\text{P}_2\text{O}_8$	Total.	$\text{H}_3\text{PO}_5$	$\text{H}_4\text{P}_2\text{O}_8$	Total.
10	0.0594	1.7	1.54	9.2	8.36	17.56	0.969	1.494	2.463
15	0.0932	3.25	3.48	11.19	11.98	23.17	1.853	3.376	5.229
20	0.1209	4.79	3.73	12.73	9.92	22.65	2.730	3.618	6.348
30	0.1861	7.26	5.8	12.54	10.00	22.54	4.138	5.626	9.704
40	0.2378	10.07	6.83	13.6	9.22	22.82	5.740	6.625	12.365
60	0.3615	11.73	7.2	10.42	6.4	16.82	6.666	6.984	13.670
120	0.7406	25.28	10.55	10.96	4.58	15.54	14.510	10.234	24.644
180	1.0920	28.48	14.7	8.37	4.32	12.69	16.234	14.259	30.493

\* Duration of electrolysis 1 hr. 40 min.

TABLE V.—THE INFLUENCE OF TEMPERATURE.

Conditions as in Table IV., the duration of electrolysis being 1 hour, but the temperature was varied. The electrolyte was practically frozen at  $-5^{\circ}\text{ C}.$ , therefore the experiments were started from  $0^{\circ}$ .

Temp. $^{\circ}\text{C}.$	Coulometer. g. Cu.	C.c. $\frac{N}{10} \times \text{Na}_2\text{S}_2\text{O}_3 - \text{Soln.}$		Current Efficiency (Per Cent.)		
		Immediately.	On the Following Day.	$\text{H}_3\text{PO}_5$ .	$\text{H}_4\text{P}_2\text{O}_8$ .	Total.
0	0.3546	12.26	8.24	11.11	7.46	18.57
5	0.3615	11.73	7.20	10.42	6.40	16.82
10	0.3621	9.68	6.57	8.59	5.83	14.42
15	0.3714	9.17	6.31	7.93	5.46	13.39
20	0.3548	5.18	5.15	4.69	4.66	9.35
25	0.3572	3.25	4.25	2.92	3.82	6.74

TABLE VI.—THE INFLUENCE OF CONCENTRATION OF AMMONIUM PHOSPHATE.

Conditions as in Table V., the temperature being about  $+5^{\circ}\text{ C}.$ , but the concentration of ammonium phosphate was varied. Electrolyte alkaline in each case. More than 4*M*-ammonium phosphate could not be dissolved.

Concn. of Ammonium Phosphate ( <i>M</i> ).	Coulometer g. Cu.	C.c. $\frac{N}{10} \times \text{Na}_2\text{S}_2\text{O}_3 - \text{Soln.}$		Current Efficiency (Per Cent.)		
		Immediately.	On the Following Day.	$\text{H}_3\text{PO}_5$ .	$\text{H}_4\text{P}_2\text{O}_8$ .	Total.
1	0.3615	11.73	7.20	10.42	6.40	16.82
3	0.3710	21.54	25.24	18.65	21.85	40.50
4	0.3746	16.38	30.71	14.05	26.34	40.39

TABLE VII.—THE INFLUENCE OF CONCENTRATION OF AMMONIUM FLUORIDE ON 3 *M* SECONDARY AMMONIUM PHOSPHATE.

Ten c.c. of solution containing 3 *M* secondary ammonium phosphate and 0.0032 g. of ammonium chromate electrolysed each time with the required amount of ammonium fluoride at about  $+5^{\circ}\text{ C}.$  with anodic C.D. of 0.01645 amp./cm.<sup>2</sup> for an hour.

Concn. of Ammonium Fluoride ( <i>M</i> ).	Coulometer g. Cu.	C.c. $\frac{N}{10} \times \text{Na}_2\text{S}_2\text{O}_3 - \text{Soln.}$		Current Efficiency (Per Cent.)		
		Immediately.	On the Following Day.	$\text{H}_3\text{PO}_5$ .	$\text{H}_4\text{P}_2\text{O}_8$ .	Total.
0	0.3714	0.93	9.53	0.80	8.26	9.06
1.1	0.3710	21.54	25.24	18.65	21.85	40.50
2.1	0.3422	25.60	29.88	24.09	28.05	52.14
3.3	0.3077	34.16	31.68	29.84	27.67	57.51
3.8	0.3747	36.22	27.30	31.05	23.40	54.45
4.8	0.3726	35.95	28.08	31.00	24.21	55.21
6.1	0.3694	35.19	24.73	30.60	21.50	52.10

TABLE VIII.—THE INFLUENCE OF CONCENTRATION OF AMMONIUM FLUORIDE ON 4 M SECONDARY AMMONIUM PHOSPHATE.

Ten c.c. of solution containing 4 M secondary ammonium phosphate, 0.0032 g. of ammonium chromate and the requisite amount of fluoride electrolysed each time under the conditions mentioned in Table VII.

Concn. of Ammonium Fluoride (M.)	Coulometer g. Cu.	C.c. $\frac{N}{10} \times \text{Na}_2\text{S}_2\text{O}_3$ - Soln.		Current Efficiency (Per Cent.)		
		Immediately.	On the Following Day.	H <sub>3</sub> PO <sub>4</sub>	H <sub>4</sub> P <sub>2</sub> O <sub>8</sub>	Total
1.3	0.3746	16.38	30.71	14.05	26.34	40.39
3	0.3753	26.04	35.29	22.29	30.20	52.49
4	0.3703	30.29	34.39	26.27	29.83	56.10

TABLE IX.—THE INFLUENCE OF CONCENTRATION OF AMMONIUM CHROMATE.

Ten c.c. of solution containing 4 M secondary ammonium phosphate and the requisite amount of ammonium chromate (in the form of ammonium dichromate solution, 5 c.c. of which corresponded to 0.0032 g. of ammonium chromate) electrolysed each time under the conditions mentioned in Table VII.

Concn. of Ammonium Dichromate Solution (C.c.)	Coulometer g. Cu.	C.c. $\frac{N}{10} \times \text{Na}_2\text{S}_2\text{O}_3$ - Soln.		Current Efficiency (Per Cent.)		
		Immediately.	On the Following Day.	H <sub>3</sub> PO <sub>4</sub>	H <sub>4</sub> P <sub>2</sub> O <sub>8</sub>	Total
2	0.3734	0.41	6.18	0.35	5.43	5.78
5	0.3714	0.93	9.53	0.80	8.26	9.06
10	0.3785	1.34	5.6	1.12	4.75	5.87

#### Attempts to Prepare Solid Ammonium Perphosphate.

According to these investigations the most favourable conditions for the formation of ammonium perphosphate in solution are: 4M (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, 3M NH<sub>4</sub>F, 0.32g. of (NH<sub>4</sub>)<sub>2</sub>CrO<sub>4</sub> per lit., anodic current density about 0.0146 amp./cm.<sup>2</sup>, temperature 0° C., duration of electrolysis from the point of view of efficiency, about 10 minutes, but from the consideration of the yield, the longer the duration the greater the yield.

Ten c.c. of electrolyte of the above composition were electrolysed under the above conditions for 3 hours. The solution showed the same reactions as a freshly prepared solution of rubidium and caesium perphosphates. It did not give a black precipitate with silver nitrate solution, but a whitish one, which soon turned yellow with evolution of ozonised oxygen (*cf.* ammonium persulphate). The solution did not evolve bubbles of oxygen as do the corresponding solutions of rubidium and caesium, indicating that the smaller alkalinity of ammonium phosphate solutions favours the stability of the permonophosphate.

When the electrolysed solution was evaporated at room temperature in a vacuum over fused calcium chloride or sodium hydroxide, even the fourth crop of crystals consisted chiefly of phosphate, while the perphosphate concentrated in the mother liquor. After separating the crystals the

residual mother liquor dried to a residue containing a little ammonium perphosphate mixed with phosphate, chromate, and fluoride. The dry residue did not liberate iodine immediately from a neutral or an acidified solution of potassium iodide, but gave all the other reactions of a freshly electrolysed solution.

Ammonium perphosphate did not crystallise out even when the electrolyte was kept saturated during electrolysis by keeping it in contact with solid ammonium phosphate contained in an ebonite tube pierced with a number of holes.

Precipitation of the freshly electrolysed solution did not give good results; 96 per cent. alcohol and silver nitrate solution precipitated both the phosphate and the perphosphate, while glacial or dilute acetic acid gave no precipitate. Barium carbonate did not precipitate the phosphate. Barium hydroxide precipitated all the impurities, phosphate, fluoride, and chromate, giving a filtrate containing active oxygen. The filtrate was freed from ammonia by a current of air and placing at ordinary temperature in a vacuum over concentrated sulphuric acid. A current of carbon dioxide was then passed and the precipitated barium carbonate filtered off. The resulting filtrate contained only traces of active oxygen. The perphosphate probably decomposed during this lengthy process.

#### *Thallium.*

Ten c.c. of solution containing about 0·5 M thallium fluoride were saturated with secondary thallium phosphate; and the solution so obtained was electrolysed with a diaphragm of parchment paper (since thallium chromate is insoluble) at 0° C., with an anodic current density of 0·0125 amp./cm.<sup>2</sup>

In about 10 minutes spongy lumps of bluish white crystals of metallic thallium separated around the diaphragm and in the electrolyte. The solution originally alkaline reacted acid, and contained no active oxygen. Electrolysis of thallous sulphate gave similar results.<sup>13</sup>

#### **Conclusions and Summary.**

1. Perphosphoric acids are not obtained by the action of 30 per cent. hydrogen peroxide at 0° C. on phosphorus oxychloride.

2. Most of the alkali and alkaline earth phosphates react with hydrogen peroxide, giving definite compounds containing hydrogen peroxide of crystallisation. Primary phosphates of lithium, ammonium, calcium, and strontium, and phosphates of thallium, however, do not react with hydrogen peroxide, while tertiary potassium phosphate decomposes it.

3. Apparently there is no relationship between water of crystallisation and hydrogen peroxide of crystallisation. Some phosphates containing no water of crystallisation, give compounds containing hydrogen peroxide of crystallisation.

4. There seems to be some relation between the alkalinity of the phosphate and the formation of compounds containing hydrogen peroxide of crystallisation. Acid-reacting phosphates, such as primary phosphates, do not react with hydrogen peroxide or else give very unstable compounds. Slightly acid-reacting phosphates like secondary phosphates of alkaline earths give unstable compounds. Alkaline phosphates, for example, secondary phosphates or pyrophosphates of alkalis give rather stable

<sup>13</sup> Crookes, *Proc. Roy. Soc.*, 1862, 12, 153; *Chem. News*, 1863, 7, 290; *J.C.S. (2)*, 1864, 2, 132.

compounds, while strongly alkaline phosphates, like tertiary potassium phosphate decompose hydrogen peroxide.

5. Electrolysis of orthophosphoric acid or of phosphates of lithium, sodium, and thallium, does not give rise to perphosphates, while secondary phosphates of potassium, rubidium, caesium, and ammonium produce on electrolysis two perphosphates in solution, namely permonophosphate and perphosphate.

Electrolysis was carried out with a low anodic and a high cathodic current density, at a low temperature, in the presence of a little chromate to prevent cathodic reduction. In the case of rubidium and caesium, perphosphates may be obtained even without the addition of fluoride, but potassium and ammonium do not give perphosphates even with such addition.

6. Ammonium perphosphates can be obtained in solution with an increased current efficiency of over 57 per cent., by using a 4 M solution of secondary ammonium phosphate, containing 3 M ammonium fluoride and 0.32g. of ammonium chromate per lit., at 0° C., with an anodic current density of about 0.0146 amp./cm.<sup>2</sup>

7. The current efficiency for production of perphosphate by electrolysis of alkali phosphate without the addition of fluoride shows an interesting relation to the atomic volume of the alkali metal. Hydrogen, lithium, and sodium do not give rise to perphosphates. Potassium does not produce perphosphates except in the presence of fluoride, but with the increase of atomic volume the tendency towards perphosphate-formation increases. Thus, rubidium gives a current efficiency of 12.32 per cent. and caesium a current efficiency of 22.33 per cent.

8. As a result of a comparative study of the two sets of products, one obtained by electrolysis and the other by the action of hydrogen peroxide on the same phosphate, it is established that the compounds obtained by electrolysis are *true perphosphates*, while those prepared by the action of hydrogen peroxide are *products containing hydrogen peroxide of crystallisation*.

In conclusion, one of the authors (S. H.) desires to thank H.E.H. The Nizam's Govt. of Hyderabad-Du. (India) for a scholarship, which enabled him to carry out this work. He is also indebted to the Chemical Society for a grant, which partly defrayed the cost of materials required in this investigation.

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## THE THERMAL DECOMPOSITION OF HYDROGEN PEROXIDE IN AQUEOUS SOLUTIONS.<sup>1</sup>

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Although the thermal decomposition of hydrogen peroxide in liquid solutions has been extensively studied, it is only recently that sufficient attention has been paid to the degree of purity of the peroxide.

<sup>1</sup> Communicated by Professor W. C. M. Lewis.

Twelve years ago, Clayton,<sup>2</sup> working in this Laboratory investigated the kinetics of the decomposition of hydrogen peroxide under conditions in which particular attention was paid to the purity of the water. Clayton concluded that the presence of organic colloidal matter, even in minute amounts, exerted an appreciable effect. Clayton, however, employed Merck's perhydrol as a source of the reactant. It is now known, particularly in the light of F. O. Rice's researches, that such material, which contains inhibitors, is an unsuitable source.

The most valuable contributions to the subject of hydrogen peroxide decomposition are those of F. O. Rice,<sup>3</sup> Rice and Rieff.<sup>4</sup> Using hydrogen peroxide, free from preservative, this author has established the following points :—

- (a) That the thermal decomposition of hydrogen peroxide, observed in aqueous solutions, as ordinarily prepared, is due in great part to the presence of dust in solution ; efficient removal of dust renders the material very stable ;
- (b) That the reaction proceeds more rapidly on surfaces subjected to cleaning treatments than on a freshly formed surface, e.g., freshly fused glass surface ;
- (c) That the decomposition of an aqueous hydrogen peroxide solution prepared in such a manner as to be free from preservative, is a zero order reaction.

The writer has re-investigated the kinetics of decomposition, starting with Merck's perhydrol and also the decomposition of material free from preservative. The results of Rice<sup>5</sup> which became available during the course of the present work are such as to render of little value a record of the measurements with the inhibitor-containing material. Consequently, these are omitted, and the account limited to the behaviour of pure hydrogen peroxide.

In general, the results obtained confirm the main conclusions arrived at by Rice ; they are, however, in some respects, novel and serve to give prominence to certain aspects of the difficult problem regarding the true nature of the decomposition of hydrogen peroxide in aqueous solutions, notably the attempt which is here made to separate the contribution made by the dust in the solution itself from the contribution made by the surface of the vessel.

### **The Thermal Decomposition of Hydrogen Peroxide, Preservative Free, in Aqueous Solutions.**

The results obtained are given under different sections as follows :—

Section 1 deals with the decomposition of pure hydrogen peroxide, in dust free water as solvent, and in freshly fused glass reaction vessels.

Section 2 deals with the decomposition of pure hydrogen peroxide in conductivity water as solvent, and in a vessel, the walls of which are wax-coated.

Section 3 deals with the decomposition of pure hydrogen peroxide in conductivity water as solvent, and with specially cleaned glass and silica surfaces as reaction surfaces.

<sup>2</sup> *Trans. Faraday Soc.*, 11, 64, 1915.

<sup>3</sup> *J. Amer. Chem. Soc.*, 48, 2099, 1926.

<sup>4</sup> *J. physical Chem.*, 31, 1352, 1927.

<sup>5</sup> The writer desires to acknowledge with gratitude the information given personally by Professor Rice in connection with the preparation of dust-free and chemically pure hydrogen peroxide solutions.

*Section 1.—The Thermal Decomposition of Pure Hydrogen Peroxide in Dust-Free Water as Solvent.*

The method of obtaining dust-free water is that described by Martin<sup>6</sup> and employed by Rice. The pure hydrogen peroxide is prepared from pure sodium peroxide in the manner described by Rice.<sup>3</sup> The bulbs, containing the dust-free water, are freshly blown from a hard glass, and to the dust-free water in the bulbs a small quantity of a strong solution (30 per cent. to 40 per cent. by weight) of hydrogen peroxide is added, the resulting system being a dilute solution of hydrogen peroxide in dust-free water. The bulb containing the solution is connected to a constant volume manometer and the reaction followed by reading the manometer.

Under these conditions, the system, as already shown by Rice, is very stable. Such decomposition as occurred gave variable results owing to the fact that a small quantity of dust was inevitably introduced, during experimentation, into the solution.

The slowest rate of decomposition, obtained by proceeding in the manner just described, was given by a 0·25 per cent.  $H_2O_2$  solution, which at 60° C. and after a time interval of 10,000 mins. was found to have decomposed by less than 0·1 per cent.

With increase in the initial concentration of the  $H_2O_2$  in the solution, it was found that the rate of decomposition increased owing no doubt to the fact that, since it is impossible to free the peroxide itself from dust, a solution containing a high percentage of hydrogen peroxide will contain a corresponding amount of dust, causing an increased rate of decomposition.

The slowest rate of decomposition found with a 1·0 per cent.  $H_2O_2$  solution is  $0\cdot10 \times 10^{-6}$  grams  $H_2O_2$  per min. per c.c. of solution.

If no attempt be made to rid the solvent (water) from dust, then the rate of decomposition found, with a 1·0 per cent.  $H_2O_2$  solution, and with a freshly fused glass surface as reaction surface, is  $1\cdot20 \times 10^{-6}$  grams  $H_2O_2$  per min. per c.c. of solution. So that even with the partial removal of the dust content of a 1·0 per cent.  $H_2O_2$  solution, the rate of decomposition has decreased twelve times. This statement refers to a freshly fused glass vessel. With a glass surface treated with cleaning agents and consequently etched, the contribution made by the glass as is shown later in the Paper becomes quite comparable with that made by the dust.

*Section 2.—The Thermal Decomposition of Pure Hydrogen Peroxide in Conductivity Water as Solvent and in Vessels the Walls of which are Coated with Wax.*

In general, the hydrogen peroxide suffers decomposition in virtue of its molecules being adsorbed on a suitable surface comprising (*a*) the surface wall of the reaction vessel, (*b*) the surface of the dust particles inevitably present in conductivity water. This view has already been expressed by other workers.

By coating the reaction vessels with wax, the decomposition due to the adsorption of the hydrogen peroxide on the surface of the reaction vessel is largely eliminated, so that the decomposition taking place in wax-coated reaction vessels may be attributed almost entirely to the presence of dust in solution.

Small, freshly blown bulbs of 150 c.c. capacity were thoroughly cleaned and dried. The inside of these bulbs was coated with a high-melting

paraffin wax<sup>7</sup> which softened at 60° C. The wax was slightly unsaturated, so that before use, it was thoroughly washed with warm water, and was

TABLE I.

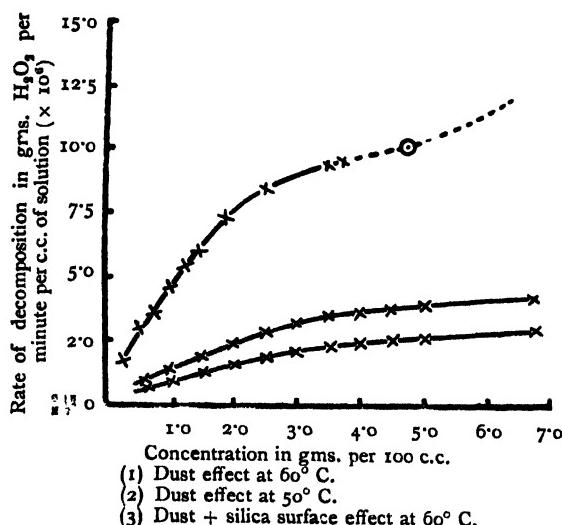
Concentration of H <sub>2</sub> O <sub>2</sub> Solution in Per Cent. (Grams per 100 c.c.)	Temp. ° C.	Rate of Decomposition in Grams of H <sub>2</sub> O <sub>2</sub> per Min. per c.c. of Solution. ( $\times 10^{-6}$ ).	Temp. Coefficient for 5° C.	Calculated Rate of Decomposition at 60° C. in Grams H <sub>2</sub> O <sub>2</sub> per Min. per c.c. of Solution. ( $\times 10^{-6}$ )
0.60	50	0.75	1.24	1.05
	45	0.605		
1.00	50	0.975	1.23	1.55
	45	0.790		
1.50	50	1.270	1.27	2.00
	45	1.000		
2.00	50	1.535	1.25	2.40
	45	1.200		
2.50	50	1.800	1.28	2.95
	45	1.400		
3.00	50	2.050	1.25	3.35
	45	1.600		
3.50	50	2.250	1.25	3.50
	45	1.800		
4.00	50	2.400	1.24	3.60
	45	1.925		
4.50	50	2.550	1.22	3.75
	45	2.100		
5.00	50	2.650	1.20	3.90
	45	2.200		

heated to 100° C. with a concentrated hydrogen peroxide solution, in order to ensure that the wax was as inactive as possible towards the hydrogen peroxide. The iodine value of the wax, before treatment, was 5.6.

In the wax-coated bulbs were placed about 60 c.c. of hydrogen peroxide solutions of various concentrations. Experiments were carried out at 45° C. and 50° C. (at these temperatures the wax was found to remain quite hard for a considerable period of time), the rate of decomposition being determined by the titration method.

(1) Dust effect at 60° C.  
 (2) Dust effect at 50° C.  
 (3) Dust + silica surface effect at 60° C.

FIG. I.



<sup>7</sup> The writer is indebted to Professor F. Francis of Bristol for information regarding the wax most suitable for the present series of experiments.

The values of  $a-x$  were plotted against the value of  $t$  (mins.), and by drawing tangents to the curves obtained the rate of decomposition corresponding to any particular bulk concentration of the  $H_2O_2$  is easily determined, both at  $45^\circ C.$  and  $50^\circ C.$

From the data so obtained, the rate of decomposition corresponding to any particular bulk concentration of the  $H_2O_2$  solution at  $60^\circ C.$  can be calculated by means of the Arrhenius equation. The results obtained by following this method of treatment are given in Table I. Taking the average value of the temperature coefficient of the reaction between  $45^\circ C.$  and  $50^\circ C.$  as  $1.24$ , the value of the critical increment of the reaction is 9,000 cals. The values of the rate of decomposition at  $60^\circ C.$  give an upper limit to the decomposition which takes place on the surface of the dust alone at  $60^\circ C.$

The values are plotted in Fig. 1. The values of the rate of decomposition at  $60^\circ C.$  are given in curve 1, the values at  $50^\circ C.$  being given in curve 2 of the same figure. It will be observed that at low concentrations there is roughly a linear relation between the rate of decomposition and concentration. At higher concentrations (above 3.0 per cent.) the rate falls off markedly.

### *Section 3.—The Thermal Decomposition of Pure Hydrogen Peroxide in Conductivity Water as Solvent.*

(A) *Silica Flask as Reaction Vessel.*—The flask was cleaned before use (a) by treatment with cold chromic acid solution, (b) by washing with cold conductivity water, (c) by a thorough steaming for 10 minutes. The water employed as solvent had an average specific conductivity of  $2 \times 10^{-6}$  reciprocal ohms.

The reaction was followed by withdrawing aliquot portions of the solution from the reaction vessel and titrating with permanganate solution in the presence of sulphuric acid.

The concentration of the hydrogen peroxide solution can be varied at will, but it is important that the initial volume of the solution be kept constant from one experiment to another.

To economise space, the tables of data obtained are not quoted. Instead, the results are shown by means of the graphs of Fig. 2. Each point of any one graph represents at least two concordant series of measurements.

In Fig. 2, the graphs numbered 1, 2, 3, 4 refer to different initial concentrations of  $H_2O_2$ , the values being 2.55, 3.6, 5.0 and 9.57 grams  $H_2O_2$  per 100 c.c. of solution respectively. From these curves the mean rate of decomposition, corresponding to any particular bulk concentration of the hydrogen peroxide, at  $60^\circ C.$ , can be obtained by drawing tangents to the above-mentioned curves. Thus curve 3 of Fig. 1 gives the mean rate of decomposition in conductivity water in a silica flask corresponding to any bulk concentration of  $H_2O_2$  solution, at  $60^\circ C.$ , between the range of concentration of 0.25 per cent. and 5.0 per cent.  $H_2O_2$ .

We have already seen that curve 1 of Fig. 1 gives the rate of decomposition, corresponding to any particular bulk concentration of  $H_2O_2$ , at  $60^\circ C.$ , such rate being due to adsorption of the hydrogen peroxide molecules on the surface of the dust. Hence by comparing curve 1 of Fig. 1, and curve 3 of Fig. 1, the values of the rate of decomposition, corresponding to any bulk concentration of  $H_2O_2$ , at  $60^\circ C.$ , due to adsorption on the surface of the silica reaction vessel, may be determined.

Following this method of analysis, the curve of Fig. 3 is obtained, which gives the rate of decomposition, corresponding to any bulk concentration of  $H_2O_2$  solution, at  $60^\circ C.$ , due to adsorption of the hydrogen peroxide molecules on the silica surface alone. Comparison of Fig. 3 with curve 1 of Fig. 1 shows that the *silica* surface is more active than the dust. It is seen from Fig. 3, that below concentrations of 1.7 per cent.  $H_2O_2$  solution, the rate of decomposition is directly proportional to the concentration of the  $H_2O_2$  solution. So that if the initial concentration of the  $H_2O_2$  solution be below 1.7 per cent. the reaction throughout its whole length will be of a unimolecular nature. Above 1.7 per cent. initial concentration of  $H_2O_2$  solution, the rate of decomposition is approximately independent of the concentration of the bulk of the solution, provided that the concentration of the bulk of the solution does not exceed 5.0 per cent., for curve 4 of Fig. 2 gives the rate of decomposition corresponding to bulk concentrations of  $H_2O_2$  solutions above 5.0 per cent. The values of the rates of decomposition, corresponding to bulk concentrations of  $H_2O_2$  above 5.0 per cent., when plotted, yield the dotted portion of curve 3, Fig. 1.

Hence the behaviour of hydrogen peroxide molecules on the surface of the silica vessel may be summarised as follows :—

The hydrogen peroxide molecules suffer decomposition in virtue of being adsorbed on the surface of the silica. The silica surface is regarded as possessing a certain number of *preformed* active points.

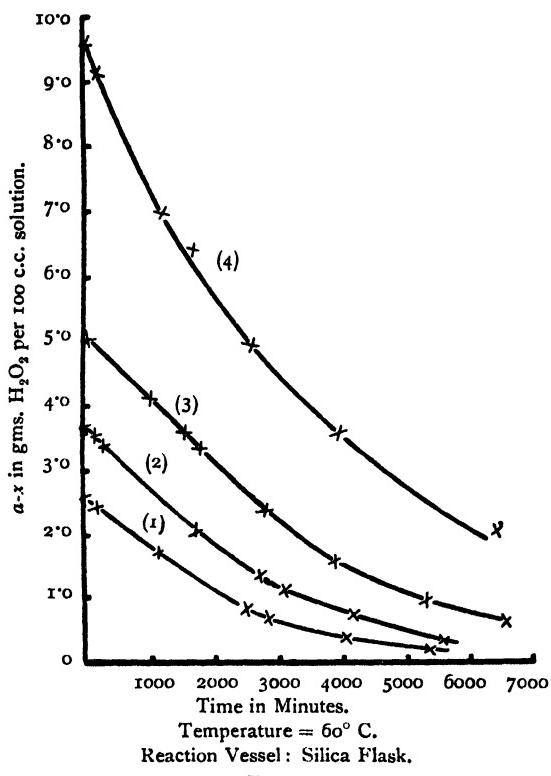
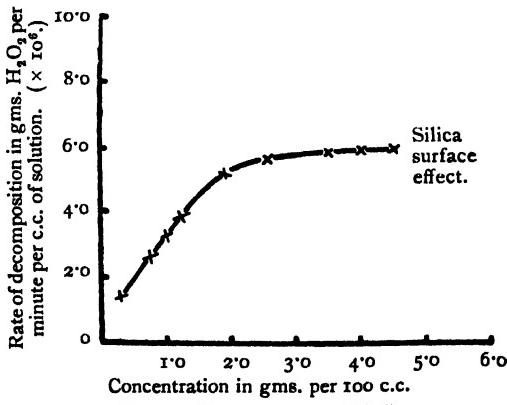


FIG. 2.

FIG. 3.—Temperature =  $60^\circ C.$

If the concentration of the hydrogen peroxide solution be below 1·7 per cent., then the silica surface is not saturated with adsorbed  $H_2O_2$  molecules, and the number of hydrogen peroxide molecules suffering adsorption will be directly proportional to the concentration of the hydrogen peroxide in the bulk of the solution.

As the concentration of the hydrogen peroxide in the bulk of the solution is increased the number of hydrogen peroxide molecules adsorbed increases, until when the concentration of the hydrogen peroxide in the bulk of the solution reaches 1·7 per cent., the silica surface becomes saturated with adsorbed  $H_2O_2$  molecules.

A further increase in the concentration of the bulk of the solution causes no further increase in the concentration of the adsorbed  $H_2O_2$  molecules, so that, above concentrations of 1·7 per cent. in the bulk of the solution, the reaction, for its primary portion, will be a zero order reaction, changing as the reaction proceeds into one of a unimolecular nature.

When, however, the concentration of the hydrogen peroxide in the bulk of the solution reaches a value above 5·0 per cent., the rate of decomposition begins again to increase with increasing concentration in the bulk of the solution.

This latter phenomenon may possibly be explained by the assumption that when the concentration of the hydrogen peroxide exceeds 5·0 per cent. other factors such as secondary adsorption films enter the reaction. Alternatively it may be explained by assuming that at sufficient concentration the  $H_2O_2$  reacts with the silica surface to produce new active points.

Experiments were also carried out at 50° C. with the silica flask as reaction vessel, and the above method of analysis is applied to the results so obtained. Knowing the rate of decomposition, due to adsorption on the surface of the silica alone, at 50° C. and 60° C. respectively, the critical increment of the silica surface process is calculated to be 17,500 calories.

(B) *Glass Flask as Reaction Vessel.*—The flask was cleaned before use, (a) by treatment with cold chromic acid solution, (b) by washing with cold conductivity water, (c) by a thorough steaming for 10 minutes. The water employed as solvent had an average specific conductivity of  $2 \times 10^{-6}$  reciprocal ohms.

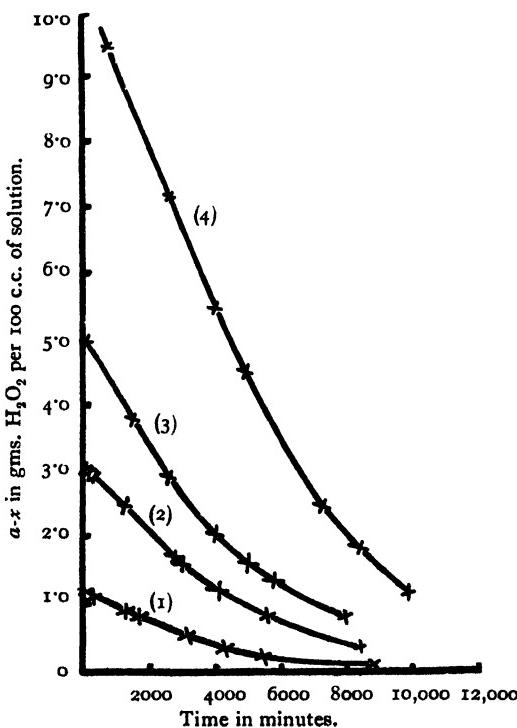


FIG. 4.—Reaction Vessel : Glass Flask.  
Temperature = 60° C.

The reaction was followed by withdrawing aliquot portions of the solution from the reaction vessel and titrating with permanganate solution in the presence of sulphuric acid. The concentration of the hydrogen peroxide solution can be varied at will, but it is important that the initial volume of the solution be kept constant from one experiment to another.

Again, to economise space, the tables of data obtained are not quoted. Instead, the results are shown by means of the graphs of Fig. 4. Each point on any one graph represents at least two concordant series of measurements.

In Fig. 4, the graphs numbered 1, 2, 3, 4, refer to different initial concentrations of  $H_2O_2$ , the values being 1.2, 3.1, 5.05, 10.3 grams  $H_2O_2$  per 100 c.c. of solution respectively. From these graphs it can be shown that for any one decomposition, the reaction, for its primary portion, is a

zero order reaction, which changes during its latter portion into one of a unimolecular nature.

In this respect, the decomposition on a glass surface resembles the decomposition on a silica surface, for it has been shown that if the initial concentration of the hydrogen peroxide solution be above 1.7 per cent., then the decomposition, for its primary portion, will be a zero order reaction, changing, during its latter portion, into one of a unimolecular nature.

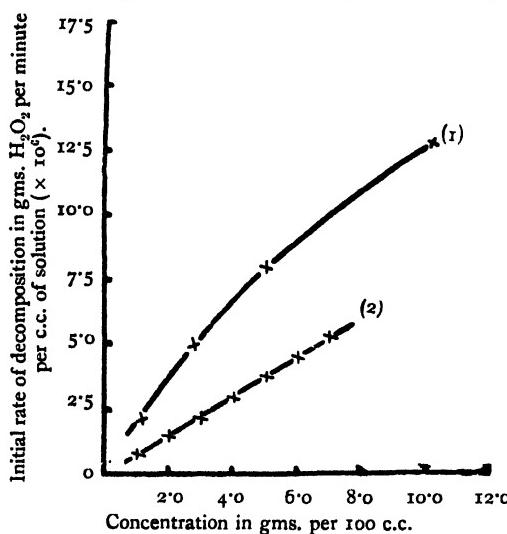


Fig. 5.—(1) Glass surface + dust effect.  
(2) Glass surface effect.  
Temperature = 60° C.

cent. and 5.0 per cent.  $H_2O_2$  solution, the initial rate of decomposition is constant), it is found that the initial rate of decomposition on a glass surface is proportional to the initial concentration of the hydrogen peroxide solution.

This is brought out more clearly by the following treatment. Fig. 5, curve 1, gives the *initial* rate of decomposition, as given by the straight line portions of curves 1, 2, 3, 4, of Fig. 4, corresponding to 1.2, 3.1, 5.05, 10.3 grams  $H_2O_2$  per 100 c.c. of solution respectively.

It will be recalled that curve 1, of Fig. 1, gave the initial rate of decomposition due to adsorption on the dust surface present in conductivity water solution, corresponding to various concentrations of hydrogen peroxide solution. Hence from curve 1 of Fig. 5 and curve 1 of Fig. 1, the initial rate of decomposition, due to adsorption of the hydrogen peroxide molecules on the glass surface alone, and corresponding to different initial concentrations of hydrogen peroxide solutions, can be calculated.

The results so obtained are shown graphically in Fig. 5, curve 2, where it is seen that the initial rate of decomposition, due to adsorption on the

In sharp contrast, however, to the decomposition on a silica surface (where it was shown, that between concentrations of 1.7 per

glass surface alone, is directly proportional to the initial concentration of the hydrogen peroxide solution.

Furthermore, it must once more be emphasised that this initial rate of decomposition can be shown to remain constant for a considerable period of time, in any one reaction, despite the diminution in the concentration of the hydrogen peroxide solution in the bulk.

These results may possibly be explained in the following manner:—

The hydrogen peroxide acts on the glass surface, in some manner, producing active catalytic points, which when once formed at the beginning of the reaction remain active throughout the particular experiment.

At the beginning of any one reaction, the active points so formed are saturated with adsorbed hydrogen peroxide molecules, so that the rate of decomposition will remain constant for a period, until when the concentration of the hydrogen peroxide in the bulk of the solution reaches a critical value (the concentration of the hydrogen peroxide suffering diminution as the reaction proceeds) the molecules of adsorbed hydrogen peroxide which suffer decomposition are no longer immediately replaced by hydrogen peroxide molecules from the bulk of the solution.

When this happens, the number of molecules of hydrogen peroxide which suffer adsorption on the active points becomes proportional to the concentration of the hydrogen peroxide in the bulk of the solution. Hence, the reaction will assume a unimolecular nature. Furthermore, the number of active points formed at the beginning of an experiment is proportional to the initial concentration of the hydrogen peroxide. On the other hand, silica behaves as though it possessed a certain number of preformed active points which remain unchanged in number over a wide range of bulk concentration of  $H_2O_2$  (up to 5 per cent.). As already pointed out, with concentrated  $H_2O_2$  the silica surface effect increases in magnitude either due to a change in type of adsorption or to the formation by the  $H_2O_2$  of fresh points.

The active points on the glass surface are of an unstable nature, for when the reaction vessels are treated, after an experiment, with cold chromic acid solution the active catalytic points are destroyed. The behaviour noted indicates that glass is chemically less resistant to  $H_2O_2$  than is silica.

Experiments were carried out with the glass flask, as reaction vessel, at  $50^\circ C.$ . The results, obtained at this temperature, were of the same type as the results obtained at  $60^\circ C.$ .

If the analysis, already outlined for the results obtained at  $60^\circ C.$ , be carried out for the results obtained at  $50^\circ C.$ , with the glass flask as re-

TABLE II.—INITIAL RATES OF DECOMPOSITION OF  $H_2O_2$  AT  $60^\circ C.$

Conditions Determining the Chemical Change.	Observed Initial Velocity in grams, $H_2O_2$ per min. per c.c. of Solution ( $\times 10^6$ ).		Critical Increment or Energy of Activation in Calories.
	Initial Concentration of $H_2O_2$ = 1 Per Cent.	Initial Concentration of $H_2O_2$ = 2 Per Cent.	
Dust surface + silica surface	4.425	7.54	13.500
Dust surface + glass surface	2.05	3.8	17.000
Dust surface alone; whence	1.30	2.3	9.000
Glass surface alone, and	0.75	1.5	23.000
Silica surface alone	3.125	5.24	17.500

action vessel, then the critical increment of the decomposition of hydrogen peroxide molecules due to adsorption on the active glass surface can be calculated. The value of this critical increment is found to be 23,000 calories.

It will be convenient at this point to summarise and illustrate the kind of results which we have been considering by collecting in tabular form the values ascribed to vessel wall and to dust respectively in two typical instances, namely 1 per cent. and 2 per cent.  $H_2O_2$  solutions. The results are given in Table II. The table likewise contains the corresponding critical increments. These are obtained from the observed individual velocities at two temperatures.

### Summary.

(1) In glass and silica reaction vessels, the thermal decomposition of pure hydrogen peroxide solutions is a zero order reaction, for the first portion of the decomposition, for all initial concentrations in the case of a glass surface, and above a limiting concentration in the case of the silica surface, the decomposition being due (*a*) to adsorption of the  $H_2O_2$  molecules on the walls of the reaction vessel, (*b*) to adsorption of the  $H_2O_2$  molecules on the surface of the dust present in solution.

(2) An upper limit to the magnitude of the decomposition, due to adsorption on the surface of the dust present in solution has been determined by using a wax vessel. The critical increment of the decomposition of this process has been found to be 9,000 calories.

(3) The adsorption of the  $H_2O_2$  molecules on the silica surface is directly proportional to the concentration of the hydrogen peroxide in the bulk of the solution, below a limiting concentration of 1·7 per cent. Between this limiting concentration of 1·7 per cent. and 5·0 per cent.  $H_2O_2$  concentration, the adsorption on the silica surface is independent of the concentration of the  $H_2O_2$  in the bulk of the solution, this being accounted for on the assumption that the surface of the silica is saturated with a unimolecular film of adsorbed  $H_2O_2$  molecules. This implies that the silica surface possesses a certain number of *preformed* active points. The critical increment of the decomposition, due to adsorption on the silica surface alone, is 17,000 calories. For still higher concentrations (above 5·0 per cent.) in the bulk of the solution, other factors are brought into play, such as secondary adsorption films.

(4) On a glass surface, any one decomposition is, for its first portion, a zero order reaction, which changes into one of a unimolecular nature, as the concentration of the hydrogen peroxide in the bulk of the solution decreases. This is due to the fact that the effective catalytic area of the glass surface and dust surface is saturated with adsorbed  $H_2O_2$  molecules for the first period of the reaction, any molecules suffering decomposition being immediately replaced by other molecules from the bulk of the solution. As the concentration of the  $H_2O_2$ , in the bulk of the solution, decreases, a point is reached when the molecules, suffering decomposition, are no longer immediately replaced by molecules from the bulk of the solution, and now the concentration of the adsorbed  $H_2O_2$  molecules becomes proportional to the concentration of the  $H_2O_2$  in the bulk. The critical increment of the process involving adsorption on the glass surface alone is 23,000 calories. Again, the initial activity of the glass surface is proportional to the initial concentration of the  $H_2O_2$  solution. This is accounted for on the assumption that the hydrogen peroxide *creates* centres

of activity on the glass surface, these active points when once formed, remaining active throughout any one decomposition. There is, therefore, a sharp contrast between the glass surface and the silica surface in regard to active points.

The author wishes to tender his thanks to the National Kitchener Memorial Fund for the grant which enabled this work to be pursued, and to Messrs. Brunner Mond & Co. for a grant to the Department of Physical Chemistry of this University.

*Muspratt Laboratory of Physical and Electro-Chemistry,  
The University of Liverpool.*

## REVIEWS OF BOOKS

### **The Interaction of Pure Scientific Research and Electrical Engineering Practice.** By J. A. FLEMING, M.A., D.Sc., F.R.S. [Pp. 235 + x with a Frontispiece and 64 figures] (London : Constable & Co. 1927. Price 15s. net).

Professor Fleming has written many books of outstanding merit, but it is doubtful whether any one of them will have appealed to a wider circle of readers than this. It contains the substance of the course of lectures delivered at the instance of the University of London in the autumn of 1926, and those who were fortunate enough to hear the lectures will remember the skill with which a vast number of facts, both theoretical and practical, were welded together to show how intimately the practice of the electrical engineer is bound up with research in the physical laboratory. The engineer, widely read in his own subject, will find the chief attraction of the book to be its straightforward exposition of those parts of the newer physical theories which bear upon so many of the modern developments of his work. Physicists and chemists will find it a mine of information concerning the technical application of many phenomena with which they have been acquainted only in the laboratory. Really the book should have been published by the Institute of Physics as a companion volume to the series of monographs on *Physics in Industry*, for it would be hard to conceive of a more impressive tribute to the importance of Physics in the workshop and factory.

Chapter I deals with electrical insulation and conduction ; it includes an account of the device used by the author to determine the body and the surface conductivities of dielectrics, as well as some suggestive remarks concerning the mechanism of conduction in metals. In Chapter II is an account of the remarkable magnetic properties of some of the iron alloys produced in recent years and a description of the discovery of hysteretic repulsion by Mr. W. M. Mordey and its application in the Mordey mineral separator. Chapter III contains the familiar story of the thermionic valve and Chapter IV deals with the glow and arc discharge. Under this heading Professor Fleming describes the action of mercury rectifiers and, in particular, the Brown-Boverie all-metal rectifier used for transforming three-phase A.C. current to direct current with an efficiency of from 85 to 90 per cent. These rectifiers, which are largely used in Switzerland, have a power output as large as 1000 kilowatts and may be used for voltages up to 5000 volts.

Chapter V. contains an account of some of the later developments in telephony and includes a description of the action and use of wave filters whereby

it has become possible to transmit as many as eighty duplexed telegraph messages and five telephone messages simultaneously over a single line. Next comes a discussion of the methods employed to cope with surges and pressure rises in transmission lines—phenomena of the utmost importance in these days of the high voltage transmission of power. Chapter VII. deals with the electric furnace and electro-chemistry in general, and the last chapter entitled *Electrical Measurement* contains an account of the technological applications of the piezo-electric properties of quartz and rochelle salt.

The treatment of these many different subjects is, of necessity, almost entirely descriptive; a detailed account would require many volumes. In every case, however, sufficient information is given to explain the principles involved and to enable the ingenuity of their application to be appreciated.

D. O. W.

**Pyrometry.** By W. P. WOOD AND J. M. CORK. (McGraw Hill Publishing Co. 1927. Pp. viii and 207. Price 15s.)

There are not too many books on pyrometry, and as befits the subject, the majority of them are both technical and technological in character.

Most of us who have had occasion to use them are fully alive to the merits of such works as that of Burgess and Le Chatelier; none the less there was need of a volume which, while losing nothing in respect of technical detail, should have something of an academic, as distinct from a technological outlook.

Such a volume is the one before us. The ground is covered thoroughly, if not exhaustively. After a discussion of temperature scales and fluid thermometers of ordinary and standard type, follows a series of chapters in which thermocouples, resistance thermometers, optical pyrometers, total radiation pyrometer and various types of recording and controlling devices are described in detail, due regard being paid to the theoretical considerations necessary for the understanding of the instruments. Two useful chapters—one on transition points and thermal analysis and one on the refractory materials used in pyrometry—conclude the book.

In a work which is confessedly academic in character it is necessary to pay more attention to logical detail than in a volume destined for the hands of the skilled technician.

One would like to see for instance a strict symbolism developed and used in such a book as this for the different scales of temperature in ordinary use; and the loose employment of the word "true" in drawing a distinction between "platinum-thermometer" temperature and "true" temperature is to be deprecated. Platinum-thermometer temperature is as "true" as any other temperature—which temperature is to be adopted as our standard is entirely a matter of definition.

The space given to liquid-in-glass thermometers is necessarily brief; still, even in the compass allotted, since the writers have elected to discuss the origin of the Fahrenheit scale, it would have been well to point out its duodecimal basis; and the discussion of elastic hysteresis might well have been followed by a description of the fixed-point technique necessary in the accurate measurement of a temperature.

Such details are, however, of relatively small importance, and the volume is one to be thoroughly recommended. A very useful feature of the book is an appendix to each chapter containing numerical examples by which the reader may test his knowledge, and suggestions for laboratory experiments for which many demonstrators will be profoundly grateful.

A. F.

## MAXIMA ON CURRENT-VOLTAGE CURVES.

### PART I.

#### Electrolysis of Nickel Salt Solutions with the Mercury Dropping Cathode.

By N. V. EMELIANOVA AND J. HEYROVSKÝ.

Received 8th October, 1927 and read 25th January, 1928.

When plotting the intensity  $i$  of the electrolytic current against the polarising *E.M.F.*, the resulting current-voltage curves ("polarisation curves") usually slope up without showing any reproducible maxima or minima. However, the special sensitive method of electrolysis with the mercury dropping cathode,<sup>1</sup> which enables us to follow cathodic processes

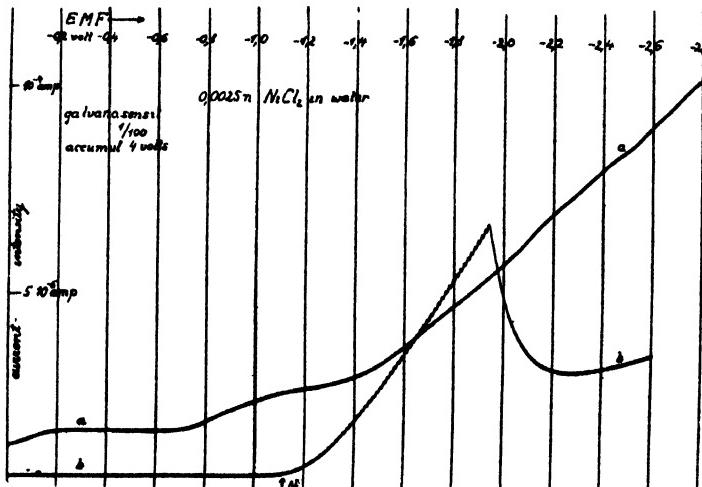


FIG. I.

and to get exactly reproducible results reveals, under certain conditions, a sudden discontinuous fall of the current. This phenomenon is specially shown when the polarisation curves are recorded automatically by means of the photographic recording instrument, the "Polarograph."<sup>2</sup>

The polarogram in Fig. I obtained with this instrument gives examples of two kinds of electrolysis in  $0.0025\text{N}$   $\text{NiCl}_2$  solution, from which, in each case, air was carefully expelled by hydrogen. For curve *a* a short platinum wire served as cathode, whilst curve *b* was obtained with the mercury dropping cathode; on the latter curve one sees the beginning of nickel deposition after 1 volt, and the prominent maximum, below 2 volts, at

<sup>1</sup> *Phil. Mag.*, **45**, 303, 1923; *Trans. Farad. Soc.*, **19**, 692, 785, 1924.

<sup>2</sup> *Rec. Trav. Chim. Pays-Bas.*, **46**, 488, 1925.

which the current suddenly falls. The nature of this phenomenon has been investigated in experiments here described. Several workers with the dropping mercury cathode have already described this phenomenon without, however, having been able to decide exactly to what mechanism the sudden decrease of current is due. Thus Shikata<sup>3</sup> investigated the conditions under which such maxima occur in the electro-reduction of nitrobenzene in aqueous solutions; Herasymenko<sup>4</sup> observed them in reductions of uranyl salt solutions; Podroužek<sup>5</sup> mentions them in his study of the reduction of quinine solutions; Sanigar<sup>6</sup> discusses the occurrence of very prominent maxima on polarisation curves of aqueous potassium-argenti-solutions.

This phenomenon has lately been observed so frequently that we must now regard the occurrence of maxima on the polarisation curves as quite general, accompanying, under certain conditions, all kathodic processes at the dropping mercury cathode. Our aim was to find the conditions which influence this phenomenon, in order to elucidate its nature from the theoretical point of view and for these investigations the typical and very suitable electro-deposition of nickel has been selected.

### Experimental.

*1. Apparatus and Arrangement.*—Fig. 2 shows the apparatus designed to eliminate air entirely from the electrolysed solution during the addition of another solution from the burette, *c*. Pure hydrogen prepared electrolytically in the Bayerle-Tamele<sup>7</sup> generator “Hydrogenogen” was passed for several hours through the wash-bottle *a* containing the solution to be electrolysed, thence into the conical electrolysing vessel *b* containing a mercury layer to serve as anode, and a funnel *g*, in which mercury dropping from the capillary cathode was collected to prevent contamination of the anode layer. The hydrogen was further passed through the rubber tubing and the open clip *d* into the burette *c* and let out through the open tap *f*, the clip *e* being closed.

Before starting the measurements, the wash-bottle *a* was inverted so that the current of hydrogen drove its contents into the electrolysing vessel *b*; the clip *d* and the tap *f* were then closed and *e* opened which allowed additions to be made from the burette to the polarised solution in an atmosphere of pure hydrogen.

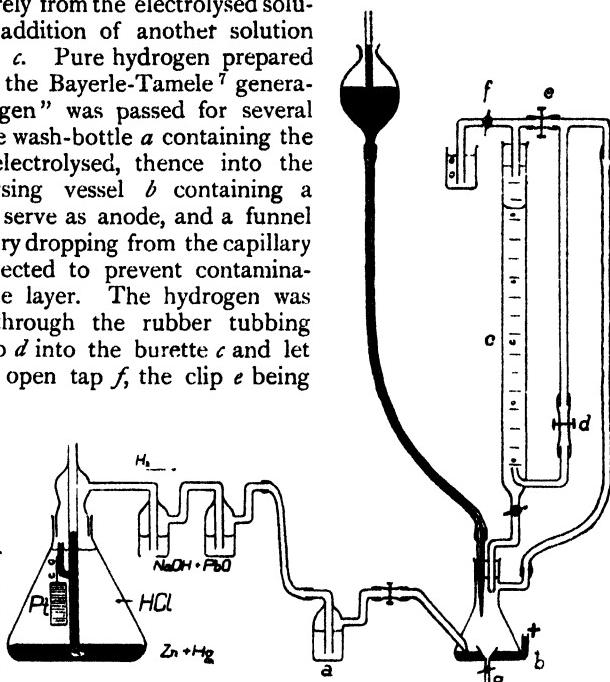


FIG. 2.

<sup>3</sup> *Trans. Farad. Soc.*, **21**, 53, 1925.

<sup>4</sup> *Rec. Trav. Chim. Pays-Bas*, **46**, 591, 1925.

<sup>5</sup> *Chem. Listy*, **18**, 389, 1924.

<sup>6</sup> *Chem. Listy*, **19**, 172, 1925.

<sup>7</sup> *Ibid.*, 496.

All current-voltage curves were obtained with the above-mentioned Polarograph, using a moving coil galvanometer (Hartmann-Braun, Frankfurt) of 100 ohms resistance and sensitivity of  $6 \times 10^{-9}$  amp.. which had often to be considerably diminished. A 2 or 4 volt lead accumulator was used as the source of the polarising *E.M.F.*

Fig. 3 shows a series of maxima observed in gradually increasing concentrations of nickel chloride; the concentration of the nickel chloride was varied by adding, to 40 c.c. of pure water in the electrolytic vessel *b*, small

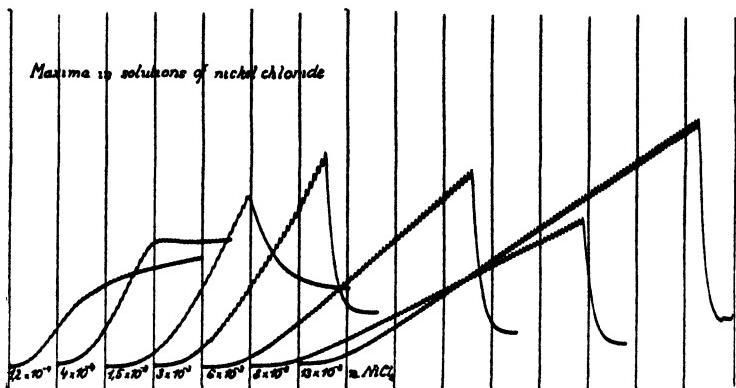


FIG. 3.

quantities of a normal solution kept carefully "reduced" by hydrogen in the burette *c*; in order to obtain maxima of about the same degree, the sensitivity of the galvanometer has to be accordingly decreased each time, since the dimensions of the apex increase considerably with the concentration of the reducible matter.

As regards the form of the curves, we observe that the proportion of the maximal current to the minimal, following thereafter, increases with the concentration. For nickel chloride solutions the following ratio was found:—

In 0.0005 <i>N</i> $\text{NiCl}_2$	almost 1 : 1
" 0.0010 <i>N</i> "	1.4 to 1.5 : 1
" 0.0025 <i>N</i> "	2.4 to 2.9 : 1
" 0.0062 <i>N</i> "	5.0 to 6.5 : 1
" 0.0100 <i>N</i> "	6.0 to 7.2 : 1.

The absolute value of the maximal current is found to increase more than the concentration; only the minimal current is strictly proportional to the concentration of the reducible ions in solution.

The influence of the rate of mercury-dropping on the current is shown in Fig. 4: the total current increases proportionally to the velocity of dropping, so that the ratio of maximum to the minimum, *i.e.* the shape of the curve remains constant. The apex is here shifted regularly towards more negative cathodic potentials. With extremely slowly dropping capillaries (one drop every 10 or 20 sec.), the maximum occurs with a considerably smaller polarising *E.M.F.*; from this it might be concluded that this phenomenon will disappear at a steady mercury cathode, its occurrence being shifted to the very beginning of deposition of nickel; indeed, polarisation curves obtained when using a small steady mercury surface as cathode, showed under exactly the same conditions, no distinct

maxima; however, it is to be noted that in these experiments no stirring was applied.

The shape of the maximum remained unchanged, however slowly or quickly the polarising *E.M.F.* were varied, continuously or discontinuously, or even if it were decreased from 2 volts to zero. These facts prove that the sudden decrease of the current is merely a function of the applied polarising *E.M.F.* and certainly does not depend on time; thus it cannot be due to exhaustion of the bulk of the solution surrounding the cathode. Various capillaries which have been employed, with varying distance from the anode mercury layer in the electrolytic vessel, gave coinciding results.

**2. The Effect of Air.**—The effect of air was detrimental; whenever the solution was exposed to air or oxygen and the solution was afterwards polarised, the maximum disappeared from the curve, leaving an ordinary "wave" as described in previous communications.

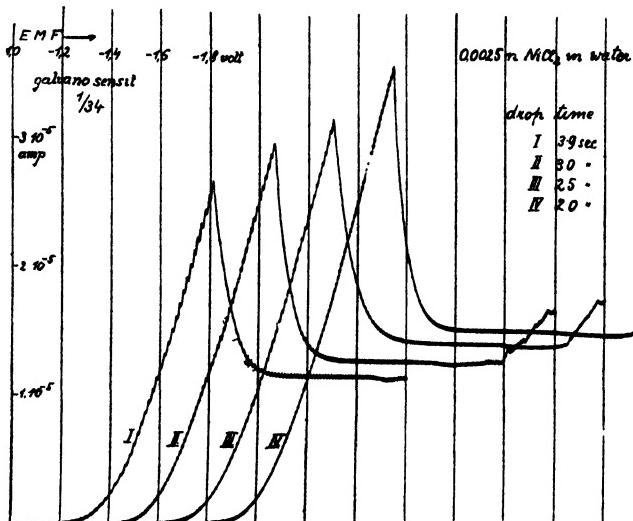


FIG. 4.

Our investigations have shown that the maximum, which becomes fully developed after two hours of bubbling hydrogen, disappeared entirely from the curve, when air or oxygen was bubbled through the solution for about one minute.

To prove that the rôle of hydrogen is merely to expel air and that it has no other influence upon the shape of the maximum, the solution in the electrolytic vessel was boiled on a glycerin bath and allowed to cool whilst tightly closed; the same maximum again appeared on the polarisation curve of this solution, now freed from air and hydrogen. The large anode (mercury layer) in the chloride solutions often acquires a considerably greater negative potential in an atmosphere of hydrogen than in air; this difference is to be ascribed to great scarcity of mercurous ions in such "well reduced" solutions. Since these solutions all show prominent maxima, the lowering effect of air upon the maxima seem to be due to the presence of mercurous ions, brought into solution by the oxidising action of atmospheric oxygen. To decide how far this explanation is valid, water saturated with

calomel and through which hydrogen had been well bubbled, was added from the burette.

Although the solubility of calomel in water is about  $10^{-6}$  molar, the suppressive effect of mercurous ions upon the maximal current is distinctly noticeable (Fig. 5). Addition of a saturated solution of mercurous sulphate (the solubility of which is  $1.2 \times 10^{-3}$  mols. per litre) was much more effective especially when this solution was run into solutions of nickel sulphate instead of into the chloride. The deleterious effect of mercurous ions on the maximal current explains also our experience that the stability of maxima is greatest in the presence of iodides, less in chlorides and least in sulphates, where the concentration of mercurous ions can be the greatest. However, mercurous solutions never suppressed the maximum completely, nor to such an extent as does the penetration of air. This indicates that air has its own particular lowering action. This action can, of course, be ascribed only to the presence of oxygen as was proved by the fact that bubbling oxygen through the solution had the same detrimental effect.

It was found, however, that a number of other substances, besides mercurous ions and air decreased the maximal current.

*3. The Suppression of the Maxima by Addition of Various Ions.*—It was soon observed that, in the presence of other electrolytes, solutions of nickel salts did not show the maxima on polarisation curves. Polyvalent kations, especially, eliminated them entirely. To study this suppressive action the following measurements were carried out:—

The aqueous solution, the suppressive effect of which was investigated, was placed in the burette *c* (Fig. 2), the nickel solution in the vessel *b*, and both solutions were carefully freed from air by bubbling hydrogen. First a concentrated solution was used in the burette, so that one or a few drops only sufficed to suppress the maximum entirely. (See e.g., Fig. 6, where three drops of a decinormal solution of aluminium chloride are already excessive.) Next the nickel solution was "titrated" with the solution in the burette suitably diluted so as to allow more exact additions: after each addition the polarisation curve was obtained and this was continued until the maximum was entirely "titrated off."

The polarogram gave thus a series of curves (see Fig. 7), each beginning at the same polarising *E.M.F.* ( $-1.0$  volt) and for clearness shifted regularly towards the right. In this manner for each nickel concentration the titrations were repeated with varying concentrations in the burette, e.g., first  $0.05$  c.c. of  $2N$   $\text{BaCl}_2$  solution sufficed to suppress the maximum in  $0.0025N$   $\text{NiCl}_2$  solution; when  $\text{BaCl}_2$  ten times as diluted (*i.e.*,  $0.02N$ ), was used  $0.45$  c.c. were necessary. Finally with  $0.002N$  solution of  $\text{BaCl}_2$

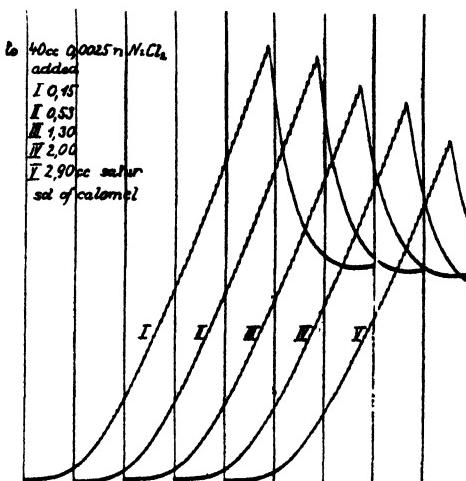


FIG. 5.

4·0 c.c. were wanted; since 30 c.cm. of the nickel solution were used, the effective concentrations of  $\text{BaCl}_2$  in the electrolytic vessel were 0·00033, 0·0003 and 0·00024, respectively. The largest of these values was regarded as the most trustworthy, since in titrations with larger quantities of solution,

complete absence of air is difficult to maintain. This circumstance as well as the uncertainty in deciding the end point of total suppression causes the results to vary within about 30 per cent.

The results of such measurements are given in the table. The solutions were prepared by weight and controlled analytically; only the purest material was used, *viz.* Kahlbaum's or Merck's "purissima" or "pro analysi."

When examining the influence of the quadrivalent thorium ion, the nitrate was dissolved in 0·003*N* HCl, in which the effect of the acid upon the maximum is negligible. It soon became apparent that the degree to which the cations suppress the maxima varies as the coagulating power of cations upon lyophobic sols, *e.g.* on colloidal arsenious sulphide. Fuchsin hydrochloride solution (1/100 and 1/10,000 molar) was therefore tried, since it is known to have a strong coagulating effect; it was found to suppress considerably.

The influence of glucose was also examined: 2·60 c.c. of a molar solution entirely prevented the formation of the maximum in 40 c.c. of 0·005*N*  $\text{NiCl}_2$ ; thus the concentration of glucose which suppresses is 0·06 molar.

Amongst other solutions, not given in the Table, the action of mercurous sulphate, thallous nitrate, and zinc chloride should be mentioned, as these did not suppress the maximal current entirely, for reasons which will be discussed below. In presence of mercurous, thallous, or hydrogen ions, nickel salts give two maxima on the polarisation curves: that of nickel as well as that due to the deposition of the other ion. The influence of anions has not been specially examined, as it seemed to matter little in this particular deposition of nickel ions.

All the measurements were carried out at room temperature of 15° to 18° C.; a special polarographic investigation at higher temperatures with

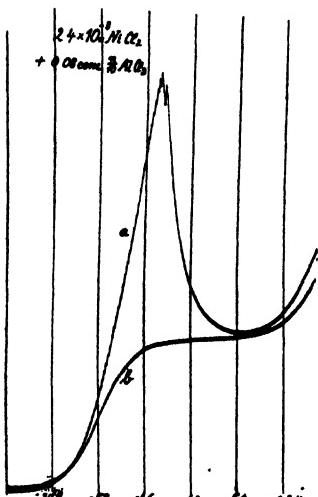


FIG. 6.

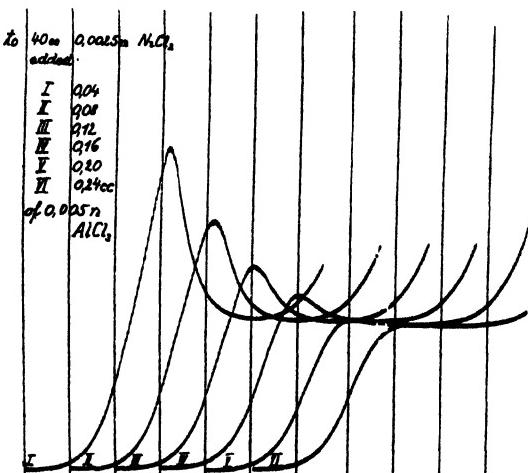


FIG. 7.

vessels in a water-bath up to 100° C., carried out by Mr. Nejedly in this laboratory, showed that the stability and prominence of maxima on polarisation curves increases with the rise in temperature.

### Discussion of the Results.

In seeking an explanation of these phenomena we have to bear in mind that all electro-reductions hitherto investigated in this laboratory with the dropping mercury method, whether inorganic or organic, simple or complex, show maxima, provided that the reducible matter is present in sufficiently large concentration. In work with several collaborators (Messrs. Berezicky, Dobrzyszycki, Herasymenko, Nejedly, Smrž, Tančákovský, Vlček and Mesdames Kačírková and Omelčenko), we noticed maxima in the deposition of the following simple ions:  $Hg_2^{2-}$ ,  $Cu^{2+}$ ,  $Tl^+$ ,  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Fe^{2+}$ ,  $Mn^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ,  $Ra^{2+}$ ,  $Na^+$ ,  $K^+$ ,  $Rb^+$ ,  $H^+$ , as well as the complex ions:  $Ag(CN)_2^-$ ,  $Cd(NH_3)_4^{2-}$ ,  $Zn(NH_3)_4^{2-}$ , Cu-tartrates, -thio-sulphides, -oxalates, *i.e.*, from complex cations as well as anions. Also in reductions of arsenious acid, molybdates, tungstates and uranyl salts, as well as in organic reductions, *e.g.*, those of nitrobenzene and quinine. Quite recently even the reduction of the oxygen dissolved in solutions which are in contact with air has been found to give prominent and most stable maxima.<sup>8</sup>

Furthermore, it is certain that the sudden fall of current is caused by the cathode itself and that it has nothing to do with the anodic process; this is evident from the indifferent rôle which the anode plays in this special electrolysis. Owing to the large surface of the anode-layer, the anodic current density is very small and the anode potential remains constant, being—according to the anion in solution—that of a reversible electrode.

Since the phenomenon of maximum accompanies all reduction processes—even mercury deposition—it cannot be explained by some special hindrance (*e.g.*, by a “cathodic passivity” as in the cases of metals of the iron triad or by “overpotential,” “gas-films,” etc.), but must be intimately connected with the manner of the reduction at the constantly renewed dropping mercury surface of the cathode. However, it is only the deposition of simple cations which has been found to be so sensitive to admixtures of polyvalent ions, as shown in the Table. Other reductions (of complex ions or organic molecules) are much less affected by the presence of electrolytes (*cf.* the results of Shikata, Herasymenko, Podroužek).

When comparing the stability of the maximum as exhibited by pure solutions of a series of cations, the maxima due to the ions of the most noble metals, mercury and copper, appear to be most stable (*i.e.*, influenced to a less degree by admixtures of other ions), than the maxima due to ions of base metals. The maxima accompanying the deposition of ions of the alkalies or alkaline earths begin to be noticeable in about centinormal solutions; those mercury or copper are well developed at  $10^{-4} N$  concentration and even in the presence of other electrolytes.

Heavier ions, again, appear to form maxima more readily than the lighter ions of the same periodic group; *e.g.*, the maximum of barium and radium is noticeable at great dilutions ( $10^{-4} N$ ), whilst that of calcium is hardly observable even at considerable concentrations.

From the physical point of view one change should be mentioned here which invariably accompanies the discontinuous fall of the maximal current

<sup>8</sup> Heyrovsky, Čas. Čs. Iékárnictva, 7, 242, 1927; Heyrovsky-Slůmek, Č. Akademie II., 36, 47, 1927.

in nickel solutions. The rate of the mercury-dropping, which during increase of the polarisation current is almost constant, increases suddenly after the maximum. One can observe this even from the polarographic curves by counting the little peaks (caused by the drops) between two abscissæ before and after the maximum. Further, the current which at the beginning of the polarisation increases exponentially with the *E.M.F.*—as is to be expected if polarisation of the cathode is complete—increases, nearer to the maximum, distinctly linearly. This shows that at the maximum the polarisation at the cathode is incomplete, *i.e.*, that the drop does not acquire fully the potential to which it is polarised. If the difference between the maximal and minimal current be denoted by  $\Delta i$  and the resistance of the electrolytic cell by  $r$  the product  $r\Delta i$  gives us the sudden increase of the kathodic potential ( $\Delta\pi$ ) after the maximum. In centinormal solutions  $\Delta i$  is about  $2 \times 10^{-5}$  amp.,  $r$  might be some hundreds of ohms, so that  $r\Delta i = \Delta\pi$  = several millivolts, if not decivolts. This explains why the drops after the maximum fall more quickly; it is a simple case of electro-capillarity owing to the change of potential. However, this physical change shows clearly that at the maximum a new process of polarisation, more complete, must suddenly set in.

The only changes at the cathode which might lead to fall of current are those of the concentration in the surface film around the mercury drop; the current after the maximum is evidently the true diffusion "saturation" current, in which the number of deposited kations depends only on the velocity of diffusion through the exhausted surface film. It is, moreover, little affected by impurities which lower the maximum (see Figs. 6 and 7). Evidently during the diffusion current considerable concentration polarisation is maintained.

The ascending branch of the maximal current indicates that the surface-layer, from which the deposited ions are recruited, must be much more concentrated at polarisations before the break in current is reached. This suggests at once that at the maximum considerable adsorption of reducible matter occurs in the surface film, which is removed at a certain value of the polarising *E.M.F.*; indeed, the maximal current is considerably larger than expected from the bulk concentration, to which the diffusion current is proportional.

That adsorption plays the decisive rôle in the formation of the maximum is further evident from the suppressive effect of small additions of electrolytes, an effect easily explained by preferential adsorption of added matter, which displaces the adsorbed nickel-ions.

**CONCENTRATIONS OF SALTS (IN G. EQ. PER LITRE) IN WHICH THE MAXIMUM IN THE  
GIVEN CONCENTRATIONS OF NICKEL CHLORIDE JUST DISAPPEARS.**

It will at once be observed from the Table (*cf.* the various amounts of electrolytes added to the 0·0025 N  $\text{NiCl}_2$  solution), that the suppressive effect of cations is identical with their coagulating effect upon negative suspensoids (*e.g.*, sol of arsenious sulphide).<sup>9</sup> The mean values of concentrations at which mono-, di- and tri-valent kations suppress the maxima, obey, in fact, Hardy-Schulze's law, that the effective dilutions ( $v_1, v_2, v_3$ ) are in the ratio 1 : K :  $K^2$ . On the whole, we see that in nickel chloride solutions monovalent cations suppress the maximum when about 40 times as concentrated as the nickel, divalent cations when present in proportion of about  $1/2\text{-}1/7$  only, and trivalent cations when they represent  $1/100\text{-}1/800$  of the nickel concentration. Thus we have the mean ratio:—

$$v_1 : v_2 : v_3 = 1/40 : 3 : 400 = 1 : 120 : 16,000,$$

which agrees with the above relationship.

However, the specific action of single cations varies; it seems that in the same group of the periodic system the heavier ions (*e.g.* Ba<sup>+</sup>) suppress the maxima in nickel solutions more readily than the lighter ions (Mg<sup>2+</sup>, Ca<sup>2+</sup>); it is to be remembered that the heavier ions alone also more readily form maxima than the lighter ones; in other words, their adsorbability being greater than that of light ions, the heavier ions displace and substitute, in the adsorption interfacial film, the less adsorbable nickel ions to a greater extent than do lighter ions. On the whole also the ions of nobler metals (Cu<sup>2+</sup>, Hg<sub>2</sub><sup>2+</sup>, Tl<sup>+</sup>) suppress the maxima of nickel solution to a greater extent than equally concentrated di- or mono-valent ions of base metals (*i.e.* of alkalies or alkaline earths). Here again it will be remembered that the deposition of nobler metals is accompanied by larger and more stable maxima than that of baser metals, which shows that the ions of nobler metals are more adsorbable than the ions of baser metals. This is in accordance with the well-known physiological "oligo-dynamic effect," explained by the excessive adsorbability of mercury and copper ions.

It is experimentally proved that next to mercurous salts,<sup>10</sup> fuchsin<sup>11</sup> shows the greatest adsorption in surfaces; our experiments confirm this, showing the very great suppressive action of fuchsin upon the maxima in nickel solutions, which must be due to the ready displacement of nickel ions by fuchsin molecules in the layer adsorbed around the mercury drop. Indeed, the suppressive activity of fuchsin almost equals that of trivalent cations.

It has been mentioned above that mercurous and thallous ions do not entirely suppress the maxima in nickel solutions, although they readily lower them; that these ions never can cause the complete disappearance of the maximum will be understood from the ready deposition of these ions at the mercury cathode: both are deposited already at a very small polarising *E.M.F.*, so that at polarisations which deposit nickel (above 1 volt) almost all the mercurous or thallous ions are already exhausted from the adsorbed cathode film, and consequently they cannot much affect the adsorption of nickel ions.

The additions of zinc-salts to solution of nickel chloride were found never to lower, but always to raise the maximum due to the deposition of ions; this behaviour is explained by the coincidence of the deposition potentials of zinc and nickel in dilute solutions; thus even if the ions of zinc replace ions of nickel in the adsorbed interfacial film, they are deposited with as much ease as the ions of nickel and thus increase the current.

<sup>9</sup> See *e.g.* H. Freundlich, *Kapillarchemie*, II. ed., p. 529.

<sup>10</sup> Schofield, *Phil. Mag.*, I, 641, 1926.

<sup>11</sup> Patrick, *Z. physik. Chem.*, 86, 545, 1914; W. C. M. Lewis, *ibid.*, 73, 129, 1910.

### Conclusions.

It is now simple to explain such changes as have been studied in these experiments and represented in Fig. 6. Curve *a* gives the ordinary maximum of a nickel-chloride solution, where the height of the maximum indicates considerable adsorption of nickel ions; after addition of two drops of  $0.1N$   $\text{AlCl}_3$  solution, the highly adsorbable trivalent aluminium ions are preferentially adsorbed around each drop to such an extent that they soon entirely displace the adsorbed nickel ions, pushing them out of the adsorption layer (according to Michaelis and Rona's or Freundlich and Losey's displacing action or Reichenstein's substitution principle). The saturation current due to diffusion of nickel ions from the bulk concentration remains then unchanged.

For the explanation of the sudden fall of current at the maximum, it has to be borne in mind that the special dropping mercury cathode provides a continually renewed and ever fresh solution-electrode interface, upon which any previous polarisation cannot leave after effects. In view of this, the cause of the sudden fall of current with increasing *E.M.F.* of polarisation has to be sought in the difference between the velocity of adsorption with which the adsorbed layer is formed round the continually fresh surface of the mercury drops, and the velocity with which kations are deposited from this layer. So long as the adsorption velocity is greater than the deposition velocity, adsorption around the mercury drop increases during the drop-formation and, thus, no concentration polarisation can arise at this cathode. However, when the polarising *E.M.F.* increases so that at the very beginning of the formation of the mercury drop the deposition of ions is greater than the adsorption, the exhaustion of the surface layer starts and consequently concentration polarisation sets in, the physical indication of which has already been discussed. An exhausted surface layer now separates the mercury surface from the bulk of the solution so that the mercury-solution interface, upon which the adsorption was built, no longer exists. The interfacial capillary forces, acting at the mercury surface, are too weak to penetrate the whole exhausted surface film and thus to cause adsorption from the interior of the solution. This removes adsorption entirely; the small current which passes after the maximum is the ordinary saturation current, entirely due to diffusion. The ascending part of the curve (Fig. 6 *a*) is thus due to the *adsorption* current, as distinguished from the *diffusion* current which occurs when the adsorption is overcome by additions of more adsorbable matter (Fig. 6 *b*) or by concentration polarisation.

Finally, we desire gratefully to acknowledge a grant from the Czech Academy of Science and Arts, to whom a report of these investigations has been communicated,<sup>12</sup> which has supported the conduct of these experiments

### Summary.

1. Polarisation curves of electro-reductions obtained with the mercury dropping cathode show very prominent maxima, the nature of which was specially studied in electro-deposition in nickel salt solutions.
2. With pure nickel salts a maximum appears only when the solutions are carefully freed from atmospheric oxygen.
3. Additions of electrolytes cause a suppression of the maximum, the suppressive effect of various cations being identical with their coagulating effect upon negative suspensoids; the effect of traces of fuchsin, also, is considerable.

<sup>12</sup> Č. Akademie II., 36, 7, 1927.

4. The phenomenon of the maximum is shown to be due to the adsorption of the reducible matter at the mercury solution interface and the suppression of maximum to be due to the replacement of the reducible ions by more adsorbable matter.

5. The sudden fall of the current after the maximum is explained by the concentration polarisation, which starts when the velocity of deposition of ions is greater than the velocity of adsorption in the surface-film at the mercury dropping cathode.

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## MAXIMA ON THE CURRENT-VOLTAGE CURVES.

### PART II.

#### The Maxima on the Polarisation Curves of Uranyl Salt Solutions.

By P. HERASYMENKO.

*Received 11th January, and read 25th January, 1928.*

The peculiar occurrence of maxima on the polarisation curves was described by M. Shikata,<sup>1</sup> E. B. Sanigar,<sup>2</sup> W. Podroužek,<sup>3</sup> and by the present author.<sup>4</sup> It is shown in Part I. that these maxima are very frequently observed during electro-reduction or deposition of various substances at the mercury dropping cathode, so that we are dealing with a new common phenomenon which seems to be of importance for the theory of polarisation.

During the first measurements with uranyl salt solutions concerning this effect the author tried to diminish the electric resistance of a dilute aqueous solution of uranyl salt in the electrolytic vessel by the addition of an indifferent electrolyte, e.g. KCl. The added salt had a marked effect on the extent of maximal current which was considerably diminished, and at still greater concentration of the added salt the maximum was entirely suppressed leaving an ordinary reduction wave. The chief attention was directed to the investigation of this suppressive action of salts.<sup>5</sup> Characteristic polarisation curves showing the influence of additions to the uranyl salt solution are represented on the polarograms Figs. 1, 2.

The maxima are found to occur on all polarisation curves obtained from pure aqueous solutions of uranyl salts hitherto studied, down to  $10^{-4}$  molar concentrations.

If we increase the polarisation the current falls, after the maximum, to a constant value which is almost independent of the concentration of other electrolytes present in solution and is proportional to the concentration of uranyl ions. This final constant current is always reached, even if the admixed electrolyte entirely suppresses the maximum on the polarisation

<sup>1</sup> *Trans. Faraday Soc.*, 21, 53, 1925.

<sup>2</sup> *Rec. Trav. Chim.*, 44, 549, 1925.

<sup>3</sup> *Ibidem*, 44, 592, 1925.

<sup>4</sup> *Chem. Listy*, 19, 5, 1925.

<sup>5</sup> A preliminary report of this striking action of salts was described in *Chem. Listy* (l.c.)

curve; it has the properties of a saturation current, due to diffusion of the reducible matter to the cathode.

The height of maximal currents in pure uranyl salt solutions is nearly

proportional to the concentration of uranyl ions.

The results of the investigation of the influence of different admixtures on the change of maximal current are shown in Fig. 3, where the concentration of the added salt, in gram-equivalents, is plotted against the magnitudes of the maximal currents ob-

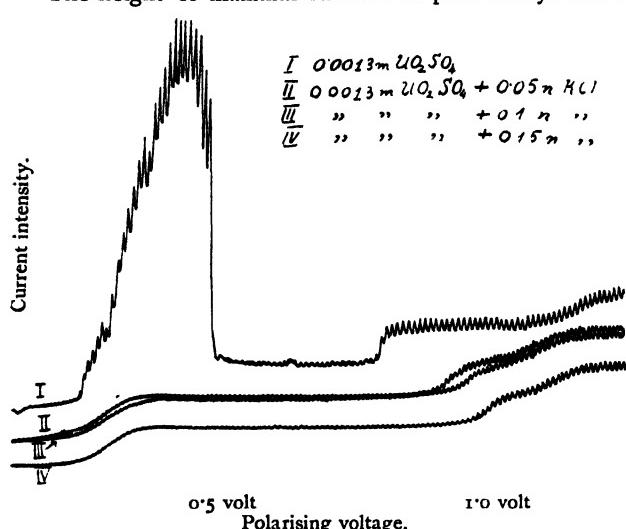


FIG. 1.—Current-voltage curves of a solution of  $\text{UO}_2\text{Cl}_2$  in different solvents.

tained. We observe that the points belonging to mono-, bi- and tervalent metallic salts fall on the same curve, which after a sudden initial increase passes through a maximum, then slowly descends and approximates to the value of the final saturation current. The fact that the maximal reduction current in pure aqueous solutions of uranyl salts is smaller than in the case of the same solution with a small addition of another salt can be explained by the increase of the electrolytic conductance.

Fig. 4 shows another set of measurements of the suppressive action of added salts; here,

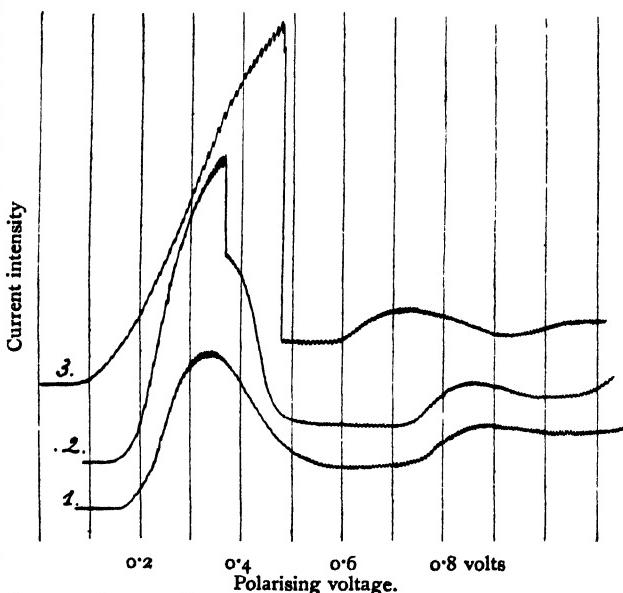


FIG. 2.—Current-voltage curves of 0.012 molar solution of  $\text{UO}_2\text{Cl}_2$  in solvents: 1—in N  $\text{MgCl}_2$ , 2—in 0.2 N  $\text{MgCl}_2$ , 3—in 0.04 N  $\text{MgCl}_2$ .

however, the abscissæ are the molar concentration of admixtures. No marked difference is observable in the action of potassium chloride and potassium sulphate at the same normality. It is further remarkable, that acetic acid, even when added in large amount, does not lower the maximal current. Since acetic acid is a weak electrolyte, the concentration of hydrions in its solutions is sufficient to increase slightly the conductance of the uranyl salt solution (and indeed the current is hereby increased), but it is too small to produce a suppression of the current.

Some non-electrolytes give an appreciable effect, especially prominent with sugar additions. The curve on the  $i - c$  diagram corresponding to sucrose additions shows a regular exponential decrease, which is due to the circumstance that in the case of non-electrolytes the conductance of solutions remains almost unaltered so that we observe only the specific suppressive action.

From the very steep decrease of the current after the maximum, observable especially in the absence of other electrolytes, in solutions of uranyl salts we may conclude that the cathode potential (which can amount to some deci- or centivolts in more concentrated solutions) also changes discontinuously. This conclusion is supported by measurements of the surface tension of the cathodically polarised mercury.

FIG. 3.

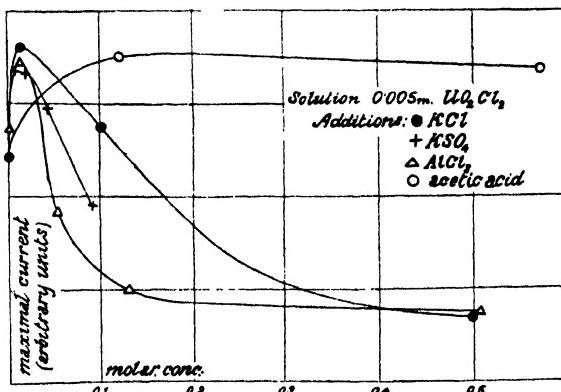
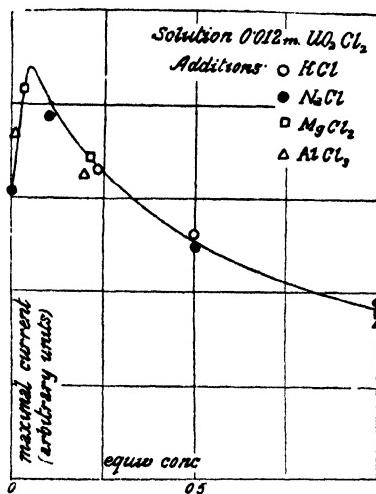


FIG. 4.

rectly in solution. At every polarising E.M.F. one hundred drops of mercury from the cathode in the solution were collected in a glass cup connected by a thin wire to the arm of a sensitive balance. A large surface of mercury at the bottom of the beaker served as anode. The air was expelled from the solution by bubbling hydrogen through it for several

<sup>6</sup> Kučera, *Ann. Physik.*, II, 529, 1903.

hours. To protect the solution from air the solution was covered with a layer of paraffin oil. The arrangement was controlled by the determination of electrocapillary curves in a normal potassium chloride solution. A parabola was obtained agreeing well with the measurements of other workers.

The electrocapillary curves from uranyl salt solutions have the shape of a deformed parabola. The deformations occur at those polarising voltages at which the rapid increases of current take place. A set of measurements made in a solution containing  $9 \times 10^{-3}$  mols. of uranyl salt with varying amounts of potassium chloride is represented in the thicker curves in Fig. 5; the thinner curves are the corresponding current voltage

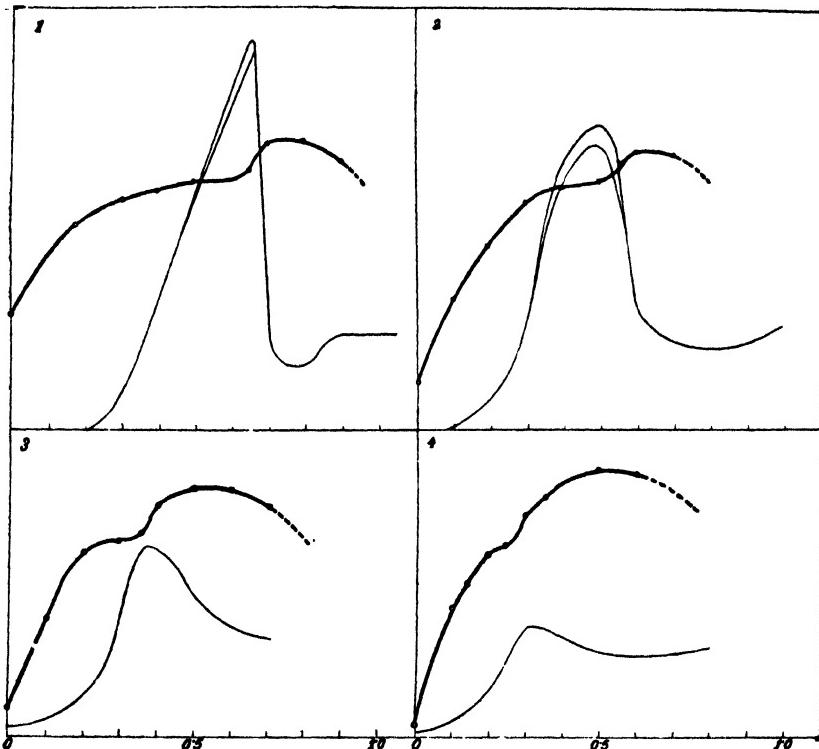


FIG. 5.—Electrocapillary and current voltage curves of  $0.009$  molar solution of  $\text{UO}_2\text{Cl}_2$  in different solvents: 1—in water, 2—in  $0.01$  N KCl, 3—in  $0.12$  N KCl, 4—in  $0.5$  N KCl. Abscissæ on these diagrams represent the polarising voltage (volts); ordinates—the interfacial tension (thicker curves) and current intensity (thinner curves).

curves. The interfacial tension is a function of the electrode potential. In the regions where the maxima on the polarisation curves occur the small variations in the interfacial tension indicate that the cathode potential does not change in the same way as the increase of polarising voltage, but lags behind. At the voltage at which the decrease of current occurs, the interfacial tension suddenly increases. This signifies that the cathode became polarisable. The further course of the electrocapillary curve follows the shape of parabola.

The presence of other electrolytes in solution causes the current to fall less abruptly, this signifying that the cathode potential changes more continuously.

It must be pointed out that the polarising *E.M.F.* corresponding to the maximum of the current is by no means constant for a given solution, but that its position changes with the speed of dropping. At the cathode which quickly renews its surface by dropping the voltage shifts towards the more negative side. This proves that we are here dealing with a process depending upon the rate of dropping and consequently with a function of current rather than of potential, as was assumed formerly by M. Shikata<sup>1</sup> and E. Sanigar<sup>2</sup> when they explained the similar effects in polarisation curves.

### Discussion.

The processes at the cathode surface may be pictured as follows. We assume that uranyl ions are adsorbed at the cathode. The electro-reduction diminishes the concentration of uranyl ions in the interfacial layer and this decrease is compensated by diffusion and chiefly by adsorption processes. We may regard the velocity of adsorption as independent of the cathode potential and may assume that the adsorption forces are negligible at some definite distance from the cathode surface. With increasing polarising *E.M.F.* the rate of exhaustion of uranyl ions from the surface layer increases, so that we reach a value of the voltage at which the diffusion and adsorption just restore the decrease of the uranyl ion concentration; at this point the current must be maximal. When, however, at any greater polarising *E.M.F.* the rate of loss of the uranyl ions is greater than the velocity of adsorption and diffusion, an exhaustion of the reducible matter must start in the interfacial film, in consequence of which polarisation sets in. Now a thin layer of a solution exhausted from uranyl ions surrounds the cathode. This layer prevents the action of adsorption forces between the cathode interface and uranyl ions in the solution, so that the reduction current suddenly falls to the saturation current, caused only by diffusion. This "film-isolation" from the adsorption forces, which now comes into play at the surface of the electrode and causes the discontinuous fall of current, must evidently depend both upon the voltage and upon the rate of dropping.

The suppressive action of additions can be explained by the hindrance of adsorption in the following manner: Since we have explained the occurrence of maxima as due to an adsorption phenomenon we should expect that the added salts would behave similarly as in other phenomena connected with adsorption, e.g., those of the coagulation of colloids; here the suppressive action should be strongly dependent on the valency of the cations of the added salt in the sense of Hardy-Schultze's rule. Indeed, such an order in the suppressive action of the cations of the added salt of different valency, corresponding to the rule mentioned, was found by N. Emelianova and J. Heyrovský in their investigation of the maxima from nickel salt solutions<sup>7</sup>

Strikingly enough in the case of the electro-reduction of uranyl salts, there is no effect observable similar to the Hardy-Schultze's rule. The suppressive action of tervalent cations is equal to that of an univalent or divalent ion if in the same equivalent concentration. Thus, here the suppressive action depends solely on the total amount of electric charges present in solution.

The explanation of this different behaviour may be sought in that circumstance that our case is complicated by the presence of products of reduction of uranyl salts, i.e., of the pentavalent uranium, which accumulates in the interfacial layer. Owing to the presence of this probably strongly

<sup>7</sup> Part I., p. 261.

adsorbed matter the specific adsorptive influences of other ions present in solution are greatly inhibited. Thus, it seems that only a large concentration of electrolytes is necessary in order to decrease the adsorption velocity of uranyl ions independently of the valency of the electrolyte.<sup>8</sup>

### Summary.

1. The maxima on the current voltage curves accompanying the first reduction stage of uranyl ions in aqueous solutions are described.
2. Additions of indifferent salts were found to have a prominent effect on the intensity of the maximal reduction current. The suppressive action depends only on the total number of electric charges in solution, so that equivalent quantities of ions of different valencies produce the same effect.
3. The intensities of the ascending currents cannot be due only to the rate of diffusion, but must also be due to the velocity of adsorption of uranyl ions.
4. The sudden decrease of current is explained by the formation of an interfacial film of solution, exhausted of uranyl ions, preventing adsorption.
5. During the increase of current the cathode potential varies only slightly with the polarising voltage; the decrease of current is accompanied by a sudden jump in polarisation of the cathode. This follows from the measurements of electro-capillary curves.

This work was carried out in the Physico-Chemical Institute of the Charles' University, Prague, and partly in the Laboratories of Ukrainian High School in Prague. For many suggestions and for his deep interest in this investigation the author is obliged to Professor J. Heyrovský, to whom the author wishes to express his best thanks.

*Prague.*

<sup>8</sup> Further development of these ideas will follow in the study of a simpler electro-reduction case, *viz.*, that of mercurous ions at the mercury cathode, investigated by J. Heyrovský, P. Herasymenko, and K. Tančákovský.

## ELECTROREDUCTION OF URANYL SALTS BY MEANS OF THE MERCURY DROPPING CATHODE.

By P. HERASYMENKO.

*Received 11th January, and read 25th January, 1928.*

Experiments on the electrolysis of uranyl salts made by the present author in 1924 showed that this electroreduction proceeds in several stages. Further investigation, the preliminary report of which was published in 1925<sup>1</sup> elucidated further the mechanism of the reduction and exhibited some remarkable polarisation phenomena of general interest.

<sup>1</sup> *Chem. Listy*, 19, No. 5, 1925.

### Experimental.

The electrolytic arrangement used in this work with the mercury dropping cathode, introduced by J. Heyrovský, was fully described in numerous papers,<sup>2</sup> so that the description of this method in detail may be omitted. The method consists in the investigation of current-voltage, "polarisation," curves, now registered automatically by means of a special photo-registering apparatus, the "polarograph."<sup>3</sup> The polarising voltage is plotted as abscissæ and the corresponding current as ordinates.

This electrolysis uses a very small mercury cathode (which steadily renews its surface by dropping from a capillary tube) and a large unpolarisable mercury anode. The use of a sensitive galvanometer (D'Arsonval type, sensitivity  $10^{-9} - 10^{-8}$  amp. per mm. of the scale from 1 meter distance), permits increase of the limits of concentrations investigated to  $10^{-5}$  g-equiv. of  $\text{UO}_2$  per litre of solution.

The solutions were prepared from uranyl sulphate and diluted by solutions of other metallic chlorides. Uranyl sulphate was obtained by evaporating a Merck's specimen of uranyl nitrate several times with purest distilled

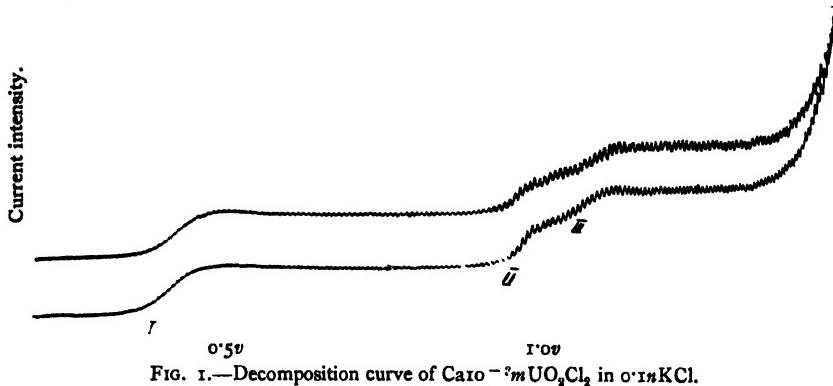


Fig. 1.—Decomposition curve of Caro -  $2\text{m}$   $\text{UO}_4\text{Cl}_2$  in  $0.1\text{n}$   $\text{KCl}$ .

sulphuric acid. The concentration of uranyl ions in solution was determined gravimetrically, as  $\text{U}_3\text{O}_8$ .

The polarisation curves obtained from these solutions show several increases of current, which correspond to different electro-chemical processes. Fig. 1 represents such a curve repeatedly obtained from the same solution. The curves are quite identical, indicating the perfect reproducibility of the results obtained by this method.

Let us regard first the increase of current which appears almost at the beginning of the polarisation curve. Since the increase of current due to starting of the electro-reduction proceeds exponentially, there is no distinct point on the curve which can be regarded as especially characteristic. In order to compare the electro-reduction from solutions of different concentrates on different curves we arbitrarily choose those points at the beginning of the reduction on different curves, which correspond to the same current intensity. The differences of potential determined by these points represent changes of the reduction potential with the concentration of the solution.

<sup>2</sup> J. Heyrovský, *Phil. Mag.*, **45**, 303, 1923; *Trans. Faraday Soc.*, **19**, 692, 1924; *Rec. Trav. Chim.*, **44**, 488, 1925; *Bull. Soc. Chim.*, **41-42**, 1224, 1927.

<sup>3</sup> J. Heyrovský and M. Shikata, *Rec. Trav. Chim.*, **44**, 496, 1925.

## ELECTROREDUCTION OF URANYL SALTS

The first conclusion to be drawn is the fact that the acidity of the solution has no influence on the cathode potential during the first reduction step as evident from the following table.

TABLE I.

Composition of the Solution.		Reduction Potential in Volts from N. Calomel Zero Corresponding to $i = 10^{-6}$ amp.
Mols. of $\text{UO}_2$	Solvent.	
$3.4 \times 10^{-3}$	0.1 N KCl	- .072
"	0.5 N HCl	- .073
$1.3 \times 10^{-3}$	0.1 N KCl	- .089
"	0.5 N HCl	- .090
"	0.86 N HCl	- .090
"	1.0 N $\text{H}_2\text{SO}_4$	- .095
$3.4 \times 10^{-4}$	0.1 N KCl	- .120
"	0.4 N HCl	- .125
"	0.8 N HCl	- .126

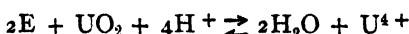
The observed values of the first reduction potential are, for a given concentration of uranyl ions, constant within the limits of experimental

TABLE II.

Molar Concentration of $\text{UO}_2$ Per Litre.	Solvent.	Reduction Potential Observed.	Mean.
0.0034	0.016 N HCl	- .071 - .075 - .072	- .073 volt
	0.1 N KCl	- .070 - .073 - .075 - .071	- .072
	0.016 N HCl	- .089 - .090 - .093	- .091
0.0013	0.01 N HCl	- .102	- .102
$3.4 \times 10^{-4}$	0.1 N KCl	- .121 - .124	- .123
$1.3 \times 10^{-4}$	0.02 N KCl	- .146	- .146
	0.1 N KCl	- .144	
	0.2 N KCl	- .148	
$8 \times 10^{-5}$	0.1 N $\text{H}_2\text{SO}_4$	- .153	- .153
	1.0 N $\text{H}_2\text{SO}_4$	- .154	
$3 \times 10^{-6}$	0.1 N KCl	- .185	- .185
$8 \times 10^{-6}$	0.1 N KCl	- .21	- .21

error and independent of the concentration of hydrions. This fact observed at the mercury cathode does not conform with the scheme proposed by

Luther and Michie<sup>4</sup> and N. Titlestad.<sup>5</sup> These authors deduce from the measurements of equilibrium potential at platinum electrodes the process:



The uncertainty of the value for the normal reduction potential found, e.g. by Titlestad, i.e.  $+0.404 \pm 0.012$  volt from hydrogen zero, shows that the evidence in favour of this reduction mechanism is insufficient.

Table II. shows that the first reduction potential of uranyl ions depends on the concentration of uranyl salts in solution.

If the observed reduction potentials are plotted against the logarithms (to the base 10) of the concentrations, a straight line is obtained the slope of which is nearly 0.057 (Fig. 2). Thus the displacements of the reduction potential with change of the uranyl concentration corresponds to a reduction process in which only one faraday per mole of uranyl is consumed.

From the independence of the potential on the acidity and the displacement of the potential with change of uranyl concentration, we conclude that the first reduction is the primary process.



The shape of the current voltage curve furnishes further evidence in favour of this scheme. The C.D. at a given potential at the beginning of the first stage of reduction at the mercury cathode is assumed to be proportional to the concentration  $c$  of the substance formed by the reduction, i.e., the pentavalent uranium, in the surface layer.

$$i = k \cdot c = k[U^{V}]$$

The adopted reaction scheme requires the relation

$$\pi = \frac{RT}{F} \log \frac{[U^{V}]}{[U^{VI}]}$$

or

$$\pi = \frac{RT}{F} \log \frac{ki}{[U^{VI}]}$$

or, for a constant concentration of uranyl ions,

$$\frac{RT}{F} \log i = \pi + \text{const.}$$

<sup>4</sup> Z. Elektrochemie, p. 826, 1908.

<sup>5</sup> Z. physik. Chemie, 72, 257, 1910.

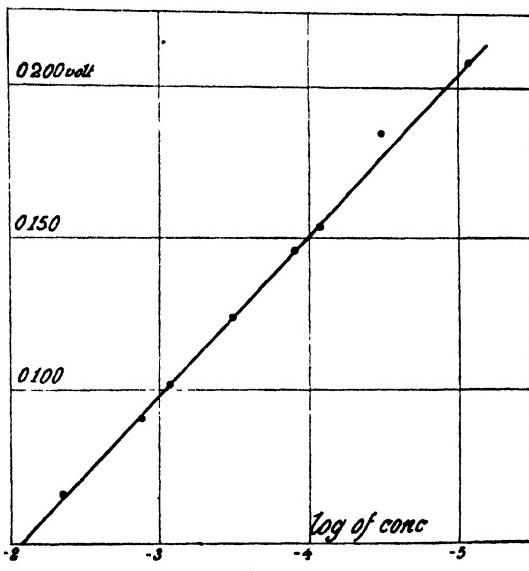


FIG. 2.

## ELECTROREDUCTION OF URANYL SALTS

This linear relation between the logarithm of current and the cathode potential is well shown in Fig. 3 obtained from the polarogram (Fig. 4). Here again, the slope of the line corresponds well with the coefficient  $\frac{RT}{F}$  (i.e., 0.058) from the above equation.

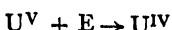
Thus, the analysis of polarisation curves obtained with the dropping mercury cathode proves the existence of pentavalency of uranium.

The possibility of the existence of compounds of pentavalent uranium is also supported by chemical facts; uranium - pentachloride ( $UCl_5$ ) is a known compound; further, Zimmermann<sup>6</sup> and also Lebeau,<sup>7</sup> when investigating the black deposit formed during electrolysis of uranyl salts, regarded this as the compound  $U_2O_5$ .

If the polarising E.M.F. is gradually increased, the current due to the first reduction increases and in very dilute solutions, in the presence of other electrolytes added to maintain uniform conductivity, we reach the saturation current (see Fig. 1). However, still further increase of the polarising voltage gives rise to a new reduction-stage, as observable from

a new sudden increase of current. With concentration above ca.  $10^{-4}$  molar solutions of uranyl salts exhibit a very remarkable polarisation phenomenon accompanying the first reduction: the current intensity after reaching a maximal value decreases with increasing polarisation (Fig. 5). The decrease of current can in no way be attributed to increase of the resistance on the surface of the electrode (e.g., in consequence of the formation of an isolating film), nor can it be caused by exhaustion of reducible matter in the bulk concentration. The surface of the steadily and regularly dropping cathode maintains its usual bright clean appearance. After the maximum the current falls to a constant value which is almost independent of the polarisation voltage and of the presence of other electrolytes in solution. This phenomenon will be discussed thoroughly in a subsequent paper.

Let us now regard the further reaction stages. On the polarisation curves (Fig. 1) we observe, after the first reduction, three other consecutive increases of current. The last increase is undoubtedly due to hydrogen evolution as evident from the value of the cathode potential.<sup>8</sup> Let us suppose that the second stage corresponds to the process



<sup>6</sup> Annalen, 232, 276, 1885.

<sup>8</sup> Herasymenko, Rec. Trav. Chim., 44, 503, 1925.

<sup>7</sup> Comp. Rendues, 174, 388, 1922.

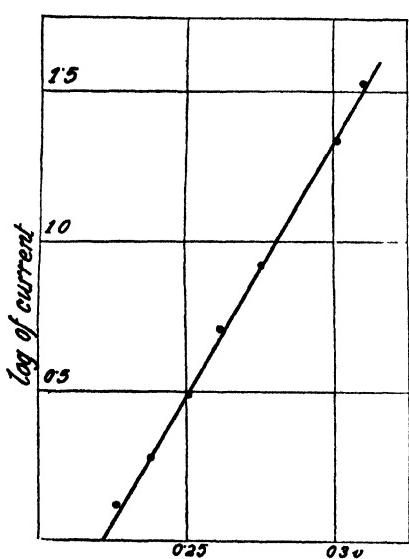


FIG. 3.

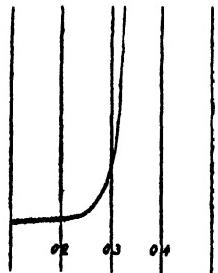
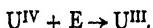


FIG. 4.

and that the third is :



These suppositions are the simplest ones since quadrivalent and tervalent compounds of uranium are well known.

This reaction scheme, further can be verified by the following experiments. A solution containing ions of quadrivalent uranium was prepared

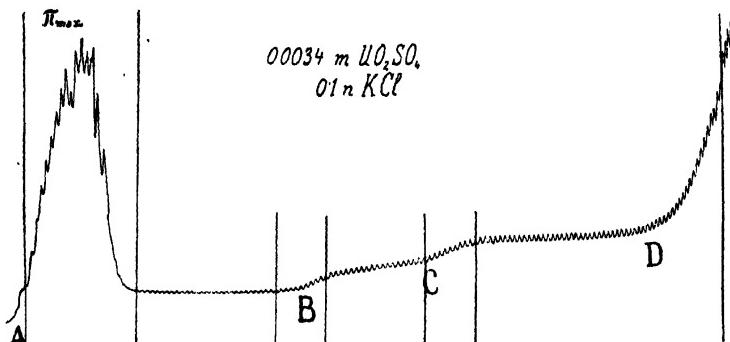


FIG. 5.

by photo-chemical reduction of an uranyl solution in presence of alcohol. The solution turned deep green and permanganate titration showed that only about  $1/6$  of the used uranyl salt remained unreduced. The polarisation curve (Fig. 6) showed that the dimensions of the polarographic "waves" corresponding to the first and second reductions are small in comparison with the third "wave." Since the height of the saturation

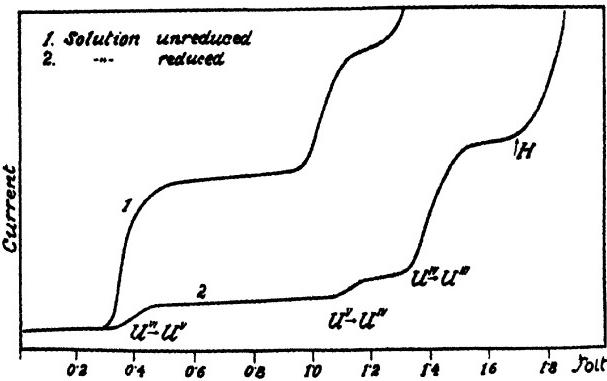


FIG. 6.

current wave indicates to a certain degree the concentration of reducible matter in solution, it becomes evident that the highest wave on the polarisation curve (third increase of current) is due to the reduction of quadrivalent uranium which is present in the solution in the greatest concentration. The last increase of the current on the polarisation curve (Fig. 6) is due to hydrogen evolution; above this stage minute bubbles of gas on the cathode surface were observed.

## ELECTROREDUCTION OF URANYL SALTS

The potentials of the second and third reduction were measured from polarisation curves which were previously mentioned. The observed values are recorded in Table III.

TABLE III.

Concentration of $\text{UO}_2$	Conc. of Other Electrolyte.	Potentials (in volts).	
		II.	III.
0.00013 mol.	0.02 N KCl	- 0.84	—
	0.05 N "	- 0.90	—
	0.2 N "	- 0.97	—
0.0013 "	0.005 N HCl	- 0.64	- 0.98
	0.05 N KCl	- 0.74	- 0.95
	0.10 N "	- 0.78	- 0.94
	0.15 N "	- 0.82	- 0.95
0.0034 "	0.005 N KCl	- 0.56	- 0.94
	0.05 N "	- 0.67	- 0.92
	0.10 N "	- 0.70	- 0.92
	0.25 N "	- 0.76	—

The exactness of these readings is smaller than in the case of the first reduction, since the readings had to be made with greater C.D.s and consequently curves could only be obtained with a considerably smaller sensitivity of the galvanometer.

We see that the third reduction potential is almost unaffected by changes of the concentration of neutral salts. However, the second reduction potential is very sensitive to neutral salt (*e.g.*, KCl,  $\text{MgCl}_2$ ) present in solution. From this behaviour of the second reduction potential, we can conclude that the pentavalent compound of uranium formed during electrolysis of uranyl salt readily forms complexes with the salts present in solution. On the contrary quadrivalent uranium exhibits no marked tendency to form complexes.

Experiments carried out in this Institute have shown that the magnitude of saturation currents on the polarisation curves is approximately proportional to the concentration of reducible matter provided indifferent electrolyses are present. Thus, since for each of the three reduction processes the same quantity of electricity is necessary, the three saturation currents corresponding to these three reactions must be equal. This is indeed observed in dilute (not too acid) solutions (see Fig. 1). But in acid solutions the saturation current due to the second reduction is smaller than the third reduction current. For this phenomenon the following explanation may be adopted: Pentavalent uranium formed in course of the first reduction is in acid solutions unstable and rapidly decomposes into hexavalent and tetravalent uranium. This decomposition is assumed to be a secondary process and its influence on the reduction current consists merely in the diminution of the concentration of pentavalent uranium and in the increase of the concentrations of hexavalent as well as tetravalent uranium. Consequently the second wave is lower than the other two.

**Summary.**

1. It has been found that the reduction of uranyl salts at the dropping mercury cathode proceeds in three stages.
2. The first reduction potential depends only on the concentration of uranyl ions, being uninfluenced by the concentration of hydrons.

3. The displacements of the reduction potential due to the dilution of uranyl ions show that uranyl ions are reduced to pentavalent uranium.

4. Two more subsequent reduction stages of uranyl salts observable at more negative potentials, are shown to be due to the processes:  $U^V \rightarrow U^{IV}$  and  $U^{IV} \rightarrow U^{III}$ ; at a still greater cathodic potential hydrogen ions finally deposit.

This work was carried out in the Physico-Chemical Institute of the Charles' University, Prague. The author wishes to express his best thanks to Professor J. Heyrovský for help and advice.

### *JOINT DISCUSSION.*

On papers by Professor HEYROVSKÝ and Mrs. EMELIANOVA (p. 257), and by Dr. HERASYMENKO (pp. 267 and 272).

**The President** remarked that as Dr. Sanigar, now working in his laboratory, had learned the use of this most interesting device in Prague, a Heyrovský dropping electrode apparatus had been set up in the Electro-metallurgical Laboratory at Sheffield, and had proved to be most useful.

**Mr. R. H. D. Barklie and Mr. F. L. Clark** said (*communicated*) that they had been interested in the results obtained by Heyrovský and his collaborators, using the Heyrovský apparatus. The papers by Emelianova and Heyrovský and by Herasymenko gave them an opportunity to direct attention to an aspect of the current-voltage curves, which seemed important.

In Heyrovský's paper in the *Bull. Soc. Chim.*, 1927, 41-42, No. 9, p. 1224, some typical polarograms relating to quantitative electro-analysis were described. In these curves, a gradual increase of applied *E.M.F.* was accompanied by a slight increase of current through the cell, up to a definite *E.M.F.* at which a very large increase of current was observed. The curve again flattened out and gave a gradual increase of current with regularly increasing applied *E.M.F.* The sudden increase of current, accompanied by very small change of applied *E.M.F.* would naturally be ascribed to a decrease in the *E.M.F.* between the solution at the cathode, and the mercury drop itself. They thought that this was of fundamental importance in the working of the apparatus, and they therefore hoped that Heyrovský and his co-workers would express their opinions upon this subject. They have not found any explanation in any of the papers they had read, nor had they found it at any time considered from this viewpoint.

They thought that a fall of cathode potential such as was postulated above might, on investigation, be found to be connected with the known change of hydrogen over-voltage corresponding to the change of cathode material. As an example of change of cathode material, they might take (1) Pure mercury being constantly renewed to form the cathode drop, (2) A very dilute zinc-mercury amalgam—the mercury being constantly renewed, and the zinc being deposited upon these drops at a fixed rate. These two cathodic compositions would correspond to the bottom and top of the curve respectively.

**Dr. Heyrovský** (*communicated*) referred to the theoretical interpretation of the aspect of the current-voltage curves he had given in an earlier

paper on the dropping mercury cathode,<sup>1</sup> as well as in the "General Introduction" to a series papers of published on the same subject.<sup>2</sup>

According to this explanation, the kathodic potential between the solution and the mercury drops was constantly and regularly increased with the increasing applied *E.M.F.*; the sudden increase of current caused by very small changes of applied *E.M.F.* was due to an increase of the deposition of cations, which formed a very dilute amalgam necessary to maintain the reversible potential at the cathode, given by

$$\pi = - \frac{RT}{nF} \log \frac{C_{\text{amalg}} \cdot K_{Me}}{[Me^n]}.$$

The flat parts of the curve were "saturation currents," due to diffusion of cations through the exhausted solution layer at the kathode; at these *E.M.F.*'s the amalgam concentration could not increase any further and the cathode potentials were there due to "concentration polarisation."

**Dr. Herasymenko (communicated)** said that there was no fall of potential during electrodeposition on a mercury cathode as postulated by Messrs. Barklie and Clark, but the cathode potential continually shifted to more negative values with gradual increase of applied *E.M.F.*

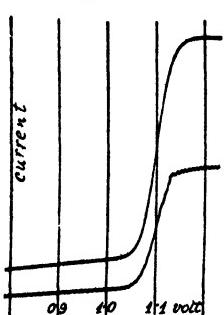


FIG. 1.—Upper curve: quickly dropping cathode. Lower curve: slowly dropping cathode.

If there were a steady mercury cathode in a solution of (e.g.)  $ZnCl_2$  then on applying an *E.M.F.* a large current would flow for the first moment. A cathode when connected to a negative pole of other source became instantly charged to this negative potential, but, since there was no equilibrium with zinc ions in solution, the latter were deposited. As soon as a dilute amalgam was formed on the cathode, an equilibrium was established and the current must fall to zero. The duration of this current, charging the mercury cathode with zinc amalgam, was very small, and such a current could hardly be observed in the arrangement described, especially if the formation of only very dilute amalgam were required to establish equilibrium.

At the dropping kathode the equilibrium between zinc ion solution and the mercury electrode was continually disturbed by the formation of a fresh mercury surface and thus the current, which tended to re-establish the equilibrium, was maintained steady (at invariable applied *E.M.F.*). This was the essential feature of polarographic measurements with Heyrovský's dropping electrode, which permitted the determination of very small traces of reducible matter in solution.

With increase of kathode potential during electrodeposition (or reduction) the current increased; the dependence of current on cathode potential was exponential, as was shown by Professor Heyrovský,<sup>1</sup> and verified in his (Dr. Herasymenko's) papers on electroreduction of uranyl salts (page 276), and maleic acid.<sup>2</sup> In these deductions no notion of over-voltage was involved and, consequently, the shape of polarisation curves had no connection with hydrogen over-voltage. It was the general experience in working with mercury dropping cathode that the deposition potential of

<sup>1</sup> *Phil. Mag.*, 45, 303, 1923.

<sup>2</sup> *Rec. Trav. Chim. Pays-Bas*, 46, 491-492, 1925, briefly summarised on p. 1229 of the *Bull. Soc. Chim.*, 41-42, 1927.

<sup>3</sup> *Z. Electrochem.*, No. 2, 1928.

hydrogen was not changed when dilute amalgams of most metals were formed on mercury. Exceptions might be found perhaps in the amalgams of noble metals (Pt, Au, Ag, Cu), but no experiments had been made on these.

It would be interesting here to point out how the sensitivity of estimation of small quantities of ions could be increased by this method.

1. Increase of temperature caused the rate of diffusion of ions to increase and, consequently, the saturation current was considerably higher. Dr. Nejedlý working at Prague<sup>4</sup> showed that at increased temperature  $10^{-7}$  g. equivalents of lead ions in solution could be easily detected. Electrolysis at high temperatures was, however, not always convenient owing to hydrolysis.

2. Increase of the rate of dropping produced an increase of current in all parts of the deposition curve. This was due to increase of the electrode surface (partly due to better stirring of the solution round the cathode). The effect of the increased rate of dropping was well shown on the polarogram (Fig. 1) representing the electrolysis of a solution containing  $10^{-4}$  g. equivalents of  $ZnCl_2$ . Here, a twofold increase of the rate of dropping resulted in a "wave" of zinc deposition which was twice as great.

<sup>4</sup> *Dissertation*, 1926, Prague.

## THE ACTIVITY OF HYDROGEN IONS IN AQUEOUS SOLUTIONS OF BERYLLIUM SULPHATE.<sup>1</sup>

BY MILDA PRYTZ.

*Received 4th January, 1928.*

It is a well-known fact that, owing to hydrolysis, aqueous solutions of beryllium sulphate show a markedly acid reaction. Using the sugar inversion method, Ley<sup>2</sup> and Bruner,<sup>3</sup> have measured the degrees of hydrolysis of various beryllium salts and compared them with the corresponding salts of iron and aluminium. Denham<sup>4</sup> has employed the hydrogen electrode to determine the degrees of hydrolysis of various salts. According to the classical theory of Nernst, the potential of the hydrogen electrode gives a means of calculating the hydrogen ion concentration in a given solution, assuming that the hydrogen ion concentration of the reference hydrogen electrode is unity (or is known). In his calculations Denham made use of the simple Nernst theory. In reality, however, the hydrogen electrode method yields a value for the relative activity of the hydrogen ion. If we assume, as the basis of our calculations, that the hydrogen ion activity of the reference (normal) hydrogen electrode is unity, we can employ the logarithmic formula of Nernst to determine hydrogen ion activities in other solutions. In the present investigation this comparative method has been followed, with the object of ascertaining the hydrogen ion activities in aqueous solutions of beryllium sulphate.

<sup>1</sup> Communicated by F. G. Donnan, F.R.S.

<sup>2</sup> H. Ley, *Z. physikal. Chemie*, **30**, 193, 1899.

<sup>3</sup> L. Bruner, *Z. physikal. Chemie*, **32**, 133, 1900.

<sup>4</sup> H. J. Denham, *J. Chem. Soc.*, **93**, 41, 1908.

### Apparatus and Method.

The measurements were made in the usual manner with potentiometer and galvanometer, using electrodes and electrode vessels of the type employed by Sørensen. The cells measured were of the two following types :—

$H_2$	BeSO <sub>4</sub> solution	3·5 <i>N</i> KCl or 1·75 <i>N</i> KCl	Hg <sub>2</sub> Cl <sub>2</sub> <i>N</i> KCl	Hg
$H_2$	BeSO <sub>4</sub> solution	3·5 <i>N</i> KCl or 1·75 <i>N</i> KCl	Hg <sub>2</sub> Cl <sub>2</sub> saturated KCl	Hg

The intermediate KCl solutions were used to eliminate the liquid potential difference according to Bjerrum's method. The difference between the observed *E.M.F.*'s with 3·5*N* KCl and 1·75*N* KCl never exceeded two millivolts and diminished rapidly with decreasing concentration of beryllium sulphate. The *E.M.F.* values given in the tables have all been corrected for the small liquid potential difference in the manner indicated. The beryllium sulphate employed was beryllium sulphuric, *puriss. cryst.* Merck (pre-war). It was carefully analysed, proved to be free from iron and aluminium, and to be the normal hydrated salt.

In the following tables and figures values are given for  $\phi_H$ , where  $\phi_H = - \log a_H$  and  $a_H$  = activity of hydrogen ion, assuming that  $a_H = 1$  for the normal hydrogen electrode at the same temperature. Values are also given for  $\alpha$ , the "percentage hydrolysis." These have been calculated on the following assumptions: (1) That the hydrogen electrode gives the concentration of hydrogen ion, *i.e.*  $\phi_H = - \log c_H$ , the concentration of hydrogen ion being taken as unity for the normal hydrogen electrode. (2) That for one hundred per cent. hydrolysis each mol. of beryllium sulphate yields one mol. of sulphuric acid. (3) That the sulphuric acid produced by hydrolysis is completely ionised. It has been thought worth while to give these values for  $\alpha$ , since the underlying assumptions will not depart too widely from the truth in the diluter solutions and thus the corresponding values of  $\alpha$  will serve to give an approximate measure of the degree of hydrolysis of the salt.

### Solutions of BeSO<sub>4</sub>.

In this series (at 25° C.) the normal calomel electrode was used.

If  $E = E.M.F.$  of cell,  $\phi_H = \frac{E - 0.2826}{0.0591}$ . The value (0.2826) for the potential difference between the normal calomel electrode and the normal hydrogen electrode at 25° was taken from the work of Lewis, Brighton, and Sebastian<sup>5</sup> and Beattie.<sup>6</sup> The results are given in Table I. (*c* = conc. of BeSO<sub>4</sub> in mols. per litre, *v* = dilution in litres per mol.).

In the case of measurements made at 40° C.,  $\phi_H$  was calculated from the equation,

$$\phi_H = \frac{E - 0.2776}{0.06209},$$

since the approximate temperature coefficient of the calomel electrode is 0.00023 volt per degree.

It will be observed that for the diluter solutions  $a_{40}$  is always greater than  $a_{25}$  for corresponding concentrations, as we should expect if  $\alpha$  gives an

TABLE I.—(SOLUTIONS OF  $\text{BeSO}_4$ .)

Temp. °C.	c.	v.	E.M.F.	$\rho_H$ .	a.
<i>Normal calomel electrode.</i>					
25	0.8636	1.16	0.3946	1.895	0.736
	0.5757	1.74	0.4087	2.133	0.639
	0.4318	2.32	0.4171	2.275	0.614
	0.2879	3.47	0.4273	2.448	0.619
	0.2159	4.63	0.4341	2.563	0.634
	0.1079	9.26	0.4489	2.813	0.712
	0.08636	11.6	0.4533	2.888	0.750
	0.05757	17.4	0.4611	3.020	0.830
	0.04318	23.2	0.4665	3.112	0.897
<i>Normal calomel electrode.</i>					
40	0.8581	1.17	0.3977	1.934	0.678
	0.5720	1.75	0.4105	2.140	0.633
	0.4290	2.33	0.4187	2.273	0.622
	0.2860	3.50	0.4291	2.444	0.635
	0.2145	4.66	0.4355	2.543	0.667
	0.08581	11.7	0.4548	2.854	0.816
	0.05720	17.5	0.4624	2.976	0.923
	0.04290	23.3	0.4679	3.065	1.004
<i>Saturated calomel electrode.</i>					
38	0.8587	1.16	0.3545	1.937	0.673
	0.4293	2.33	0.3753	2.274	0.619
	0.2862	3.49	0.3851	2.433	0.644
	0.2147	4.66	0.3922	2.548	0.659
	0.08587	11.6	0.4111	2.854	0.814
	0.05725	17.5	0.4193	2.987	0.899
	0.04293	23.3	0.4249	3.078	0.973
	0.02862	34.9	0.4323	3.198	1.11
	0.02147	46.6	0.4382	3.294	1.18

approximate measure of the degree of hydrolysis. For the more concentrated solutions, however,  $a_{40} < a_{25}$ .

As a check on the results at  $25^\circ$  and  $40^\circ$ , a series of measurements was made at  $38^\circ$  C., using a calomel electrode with saturated KCl solution. According to Michaelis, the value for the saturated calomel electrode against the normal hydrogen electrode at  $38^\circ$  C. is  $0.2350$  volt. Hence in this case  $\rho_H = \frac{E - 0.2350}{0.06169}$ . The results are given in Table I. It will be seen that for corresponding concentrations the values of  $\rho_H$  and  $a$  at  $38^\circ$  differ only slightly from those at  $40^\circ$  C.

In Fig. 1, the values of  $\rho_H$  and  $a$  ("percentage hydrolysis") for the three series of measurements have been plotted against the dilution of the  $\text{BeSO}_4$  solution.

The minima in the curves for  $a$ , which occur at relatively high concentrations, show the effect of  $\text{BeSO}_4$  in increasing the activity of the hydrogen ions produced by hydrolysis. Although the true value of the percentage hydrolysis will almost certainly diminish with increasing concentration, the increasing effect, at higher concentrations, of the ions of  $\text{BeSO}_4$  on the activity of hydrogen ion causes the apparent percentage hydrolysis (as determined electrometrically) to increase with increasing salt concentration above a certain value of the latter.

### Mixed Solutions of $\text{BeSO}_4$ and $\text{H}_2\text{SO}_4$ .

In order to throw some further light on this matter, several series of measurements were made employing solutions of pure sulphuric acid and also mixed solutions containing both beryllium sulphate and added sulphuric

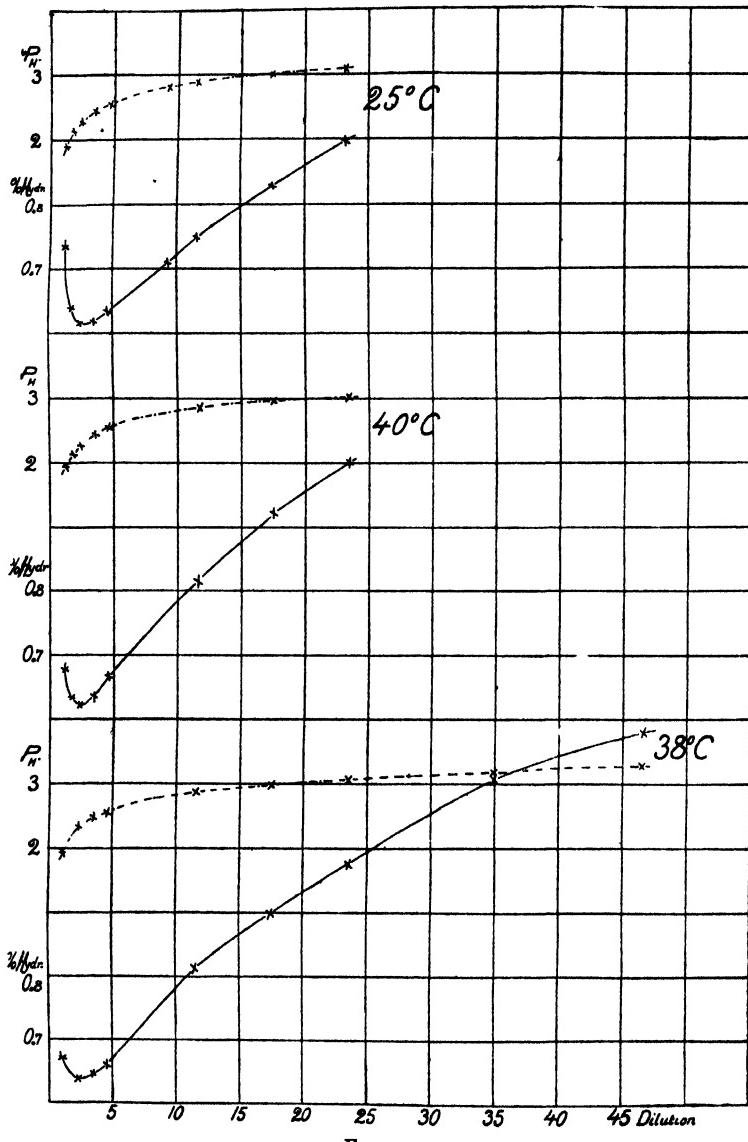


FIG. 1.

acid. The results are shown in Tables II and III. Concentrations in mols. per litre.

The results given in Tables II. and III. are shown graphically in Fig. 2 (2a and 2b).

Fig. 2a shows that for the lower concentrations of  $\text{H}_2\text{SO}_4$  the effect of

TABLE II.—SOLUTIONS OF  $H_2SO_4$  AT 38° C. SATURATED CALOMEL ELECTRODE.

Mols. of $BeSO_4$ per Litre.	$c (H_2SO_4)$ .	E.M.F.	$\rho_H$ .
0	0.00142	0.4015	2.699
	0.00184	0.3935	2.509
	0.00275	0.3826	2.392
	0.00283	0.3877	2.378
	0.00375	0.3736	2.247
	0.00472	0.3701	2.190
	0.00566	0.3650	2.107
0.2146	0	0.3922	2.548
	0.00142	0.3883	2.485
	0.00283	0.3851	2.438
	0.00566	0.3781	2.320
	0	0.3851	2.433
0.2862	0.00092	0.3829	2.397
	0.00184	0.3816	2.376
	0.00275	0.3797	2.345
	0.00367	0.3787	2.329
	0.00566	0.3750	2.269

TABLE III.— $BeSO_4$  SOLUTIONS AT 38° C. SATURATED CALOMEL ELECTRODE.

Mol. $H_2SO_4$ per Litre.	$c (BeSO_4)$ .	E.M.F.	$\rho_H$ .
0.00566	0	0.3650	2.107
	0.0143	0.3725	2.229
	0.02862	0.3757	2.281
	0.04293	0.3791	2.336
	0.2147	0.3781	2.320
	0.2862	0.3750	2.269
0.0563	0	0.3295	1.532
	0.02147	0.3326	1.582
	0.02862	0.3337	1.600
	0.04293	0.3361	1.639
	0.08587	0.3419	1.733
	0.2147	0.3465	1.807
	0.2862	0.3475	1.823
	0.4293	0.3467	1.811

added  $BeSO_4$  is to decrease  $\rho_H$  and therefore increase  $a_H$ , whilst for the higher concentrations of  $H_2SO_4$  the reverse is true. In Fig. 2b one curve shows the variation of  $\rho_H$  with concentration for pure  $BeSO_4$  solutions. The other two curves show that for solutions containing a fixed concentration of added  $H_2SO_4$  the initial effect of increasing the  $BeSO_4$  concentration is to raise the value of  $\rho_H$  and therefore diminish the value of  $a_H$ . With increasing  $BeSO_4$  concentration a maximum value of  $\rho_H$  is attained, after which further addition of  $BeSO_4$  diminishes  $\rho_H$  and thus increases  $a_H$ .

### Mixed Solutions of Magnesium Sulphate and Sulphuric Acid.

The previous measurements show the marked effect which the unhydrolysed part of the beryllium sulphate can exert on the activity of the hydrogen

## THE ACTIVITY OF HYDROGEN IONS

ions resulting from the hydrolysis of the salt. This so-called neutral salt action renders illusory any attempt to obtain by means of the hydrogen electrode an approximate estimate of the percentage hydrolysis of the salt, except in the more dilute solutions. An attempt to circumvent this difficulty

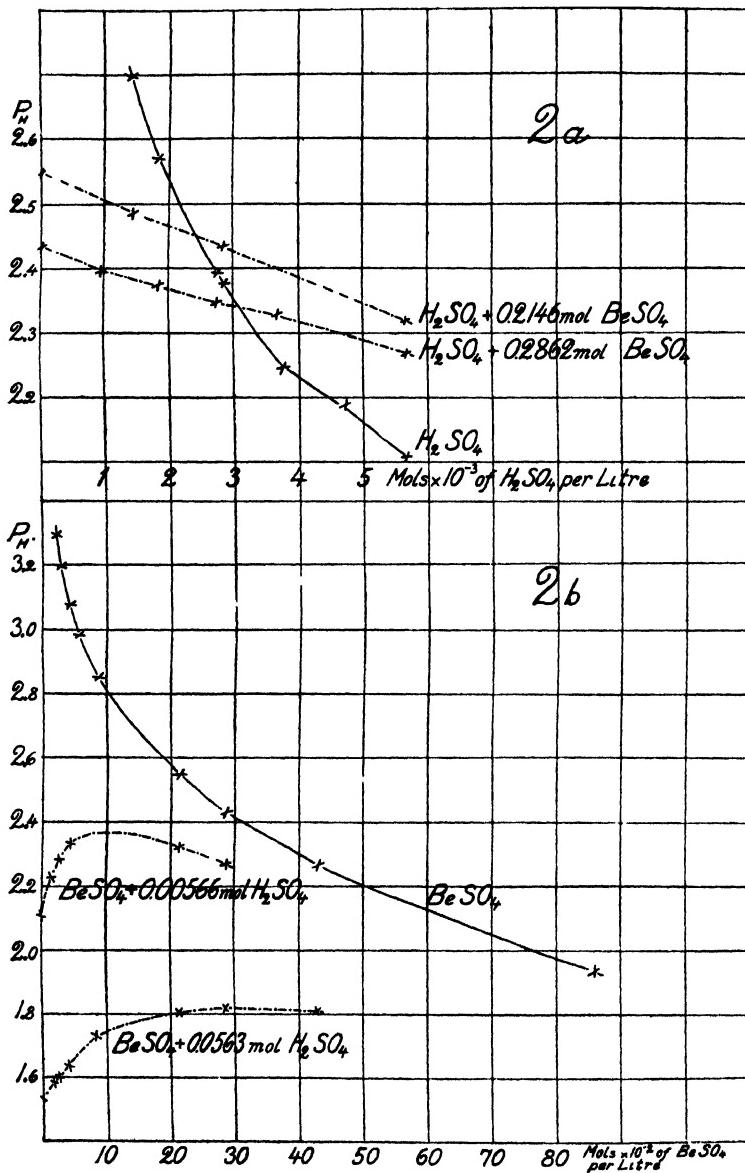


FIG. 2.

was carried out in the following manner. A series of solutions of  $MgSO_4$  were made up corresponding in molar concentration to the  $BeSO_4$  solutions referred to in Table I. The acidity of each  $MgSO_4$  solution was varied (by means of known amounts of  $H_2SO_4$ ), until it possessed the same value of

$\rho_H$  as the corresponding  $\text{BeSO}_4$  solution. Since these pairs of solutions possess the same value of  $\rho_H$ , they will also possess the same value of  $a_H$ . If we assume that the hydrolysis of  $\text{MgSO}_4$  is negligible and that the ions of  $\text{MgSO}_4$  have the same effect on the activity of the hydrogen ions as the ions of  $\text{BeSO}_4$ , then these equal values of  $a_H$  will correspond to equal values of  $c_H$ , and therefore equal values of "free  $\text{H}_2\text{SO}_4$ " (assuming complete ionisation of  $\text{H}_2\text{SO}_4$ ). Hence the known values of  $\frac{[\text{H}_2\text{SO}_4]}{[\text{MgSO}_4]} \times 100$  for the magnesium sulphate solutions should give values for the true percentage hydrolysis of the corresponding solutions of beryllium sulphate. In this mode of procedure an error must be introduced owing to the fact that the acidified solutions of  $\text{MgSO}_4$  contain a greater concentration of  $\text{SO}_4^{2-}$  ion (owing to the additional  $\text{H}_2\text{SO}_4$ ) than the corresponding solutions

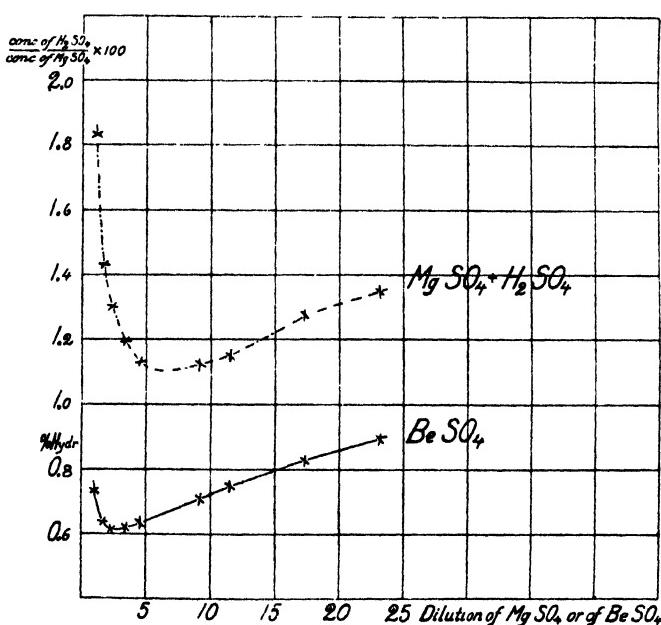


FIG. 3.

of  $\text{BeSO}_4$  of equal molar concentration. This error has been neglected, since the concentration of added  $\text{H}_2\text{SO}_4$  was usually relatively small compared with the  $\text{MgSO}_4$  concentration. An example will illustrate the experimental procedure.

A solution of 0.5757 molar  $\text{BeSO}_4$  gave  $\rho_H = 2.133$ . A solution 0.5757 molar with respect to  $\text{MgSO}_4$  and 0.01365 molar with respect to  $\text{H}_2\text{SO}_4$  gave  $\rho_H = 1.869$ , whilst a solution with the same concentration of  $\text{MgSO}_4$  but 0.008475 molar with respect to  $\text{H}_2\text{SO}_4$  gave  $\rho_H = 2.121$ . These two  $\rho_H$  values were now plotted against the  $\text{H}_2\text{SO}_4$  concentration. A small linear extrapolation indicated  $\rho_H = 2.133$  for a molar concentration of  $\text{H}_2\text{SO}_4$  equal to 0.00824. A solution made up to be 0.5757 molar with respect to  $\text{MgSO}_4$  and 0.00824 molar with respect to  $\text{H}_2\text{SO}_4$  gave  $\rho_H = 2.132$ . This procedure was repeated for each concentration of  $\text{MgSO}_4$ .

The results of the measurements and calculations are given in Table IV.

All values of  $c$  (concentration) are given in mols. per litre. The values of  $a'$  given in the last column are the values of  $\frac{[\text{H}_2\text{SO}_4]}{[\text{MgSO}_4]} \times 100$ .

TABLE IV.—SOLUTIONS OF  $\text{MgSO}_4 + \text{H}_2\text{SO}_4$  AT  $25^\circ\text{C}$ . SATURATED CALOMEL. ELECTRODE ( $e_0 = 0.2464$ ).

$c(\text{MgSO}_4)$	$v(\text{MgSO}_4)$	$c(\text{H}_2\text{SO}_4)$	<i>E.M.F.</i>	$p_{\text{H}^+}$	$a'$
0.8636	1.16	0.01581	0.3584	1.895	1.83
0.5757	1.74	0.00824	0.3724	2.132	1.43
0.4318	2.32	0.005596	0.3807	2.272	1.30
0.2879	3.47	0.003433	0.3911	2.448	1.19
0.2159	4.63	0.002438	0.3980	2.564	1.13
0.1079	9.26	0.001219	0.4129	2.813	1.13
0.08036	11.6	0.0009956	0.4170	2.886	1.15
0.05757	17.4	0.0007381	0.4250	3.022	1.28
0.04318	23.2	0.0005836	0.4304	3.113	1.35

The results in this Table are to be compared with those given in Table I. The values of  $a$  and  $a'$  are shown plotted against dilutions in Fig. 3. It will be seen that  $a'$  is always greater than  $a$ . Unfortunately the values of  $a'$  cannot be regarded as giving correct values for the percentage hydrolysis of beryllium sulphate, since the curve for  $a'$  as a function of the dilution of the beryllium sulphate shows as pronounced a minimum as the corresponding curve for  $a$ . Some of the assumptions underlying the calculation must therefore be erroneous. It is possible that the effect of  $\text{MgSO}_4$  on the activity of the hydrogen ion is very different from that of  $\text{BeSO}_4$ .

### Summary.

1. By means of the hydrogen electrode determinations of  $p_{\text{H}}$  in solutions of  $\text{BeSO}_4$  at different concentrations and temperatures have been made.
2. Corresponding determinations have been made in mixed solutions containing both  $\text{BeSO}_4$  and  $\text{H}_2\text{SO}_4$ .
3. The results of these measurements have been discussed in their relation to the hydrogen ion activities and the effect thereon of the ions of the salt.
4. By comparing solutions of  $\text{BeSO}_4$  with equimolar solutions of  $\text{MgSO}_4$  containing sufficient added  $\text{H}_2\text{SO}_4$  to yield the same values of  $p_{\text{H}}$ , an attempt has been made to ascertain the percentage hydrolysis of the solutions of  $\text{BeSO}_4$ .

My best thanks are due to Professor F. G. Donnan for suggesting this work and for his kind interest and help.

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# THE VAPOUR EQUILIBRIUM OF AQUEOUS GLYCERIN SOLUTIONS.\*

By D. F. STEDMAN.

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The original object of this investigation was a determination of the equilibrium composition of vapour and liquid at definite pressures and temperatures in the system glycerin-water. Owing to the length of time occupied by the preliminary experiments only a portion of this programme has been completed; the compositions of the vapour in equilibrium with liquid at a series of pressures and temperatures have been determined. It is hoped that the results will possess technical as well as scientific value since the composition of the (equilibrium) vapour arising from aqueous glycerin solution boiling between 50° C. and 200° C. and over the pressure range 60 mm.-760 mm. can now be stated with a fairly high degree of accuracy.

## Material Employed.

The special thanks of the author are due to the members of *The British Expert Committee on the Standardisation and Analysis of Glycerin*, who kindly supplied for this work about 50 lbs. of specially selected and highly purified glycerin. This glycerin was guaranteed to possess an absolute purity of 99·8-99·9 %, excluding water. Ordinary "pure" glycerin is useless for the present purpose, since it may contain from 2 to 3 % of organic impurities.

## Method Employed.

As different methods may be used, a considerable amount of time was spent on the consideration and testing of such methods. The one finally selected may be briefly described as follows. The vapour of glycerin and water arising from a boiling flask or still is passed through a still head kept at a constant temperature and pressure. By the regulated supply of glycerin and water (or water vapour) to the still, the composition of the liquid and hence its boiling-point (at the given fixed pressure) and the composition of the vapour arising from it are gradually and systematically altered. During this procedure samples of the distillate are analysed both before and after condensation begins in the still head. By plotting these results, the point is found when the still head neither superheats the vapour nor produces condensation. The point so found gives the composition of the vapour in equilibrium with liquid at the temperature and pressure of the still head. This method reduces to a minimum the amount of decomposition which occurs when glycerin solutions are distilled, since the quantity of glycerin present in the still at any moment need not be large and the distillation can be rapidly carried out. Determinations of acrolein (by means of a standard sensitive Schiff's reagent) in the distillate showed that many of the more usual methods are quite useless in the case of glycerin, owing to excessive decomposition.

\* Communicated by Professor Donnan.

### Apparatus.

*A. The Method of Producing the Vapour.*—After much experimenting with various forms of still, two satisfactory designs were obtained. These are both described, as each was used to make some of the measurements. The first form of still is shown in Fig. 1. The boiling flask (called the still) was blown from resistance glass and a tube for a thermometer sealed through the side, good thermal contact being secured by means of a little mercury. Although the flask was heated mainly by a gas ring burner (giving small luminous flames not touching the glass), it was also fitted with an electrically heated platinum spiral. Round the flask were placed detachable shields made of asbestos paper to prevent excessive radiation, but the tube leading to the still head required more careful lagging. As this tube is heated by the same current as the still head, it will be considered later in greater detail. During a distillation the boiling-point of

the glycerin in the still may be readily controlled by the amount of water added. Tap *a* has grooves filed partly round the plug so that the water supply can be closely adjusted, whilst exact regulation is effected by means of tap *b*. There is also an arrangement (shown in the Figure) for mixing partially cooled glycerin with the water supplied to the boiling flask. Owing to the difference in den-

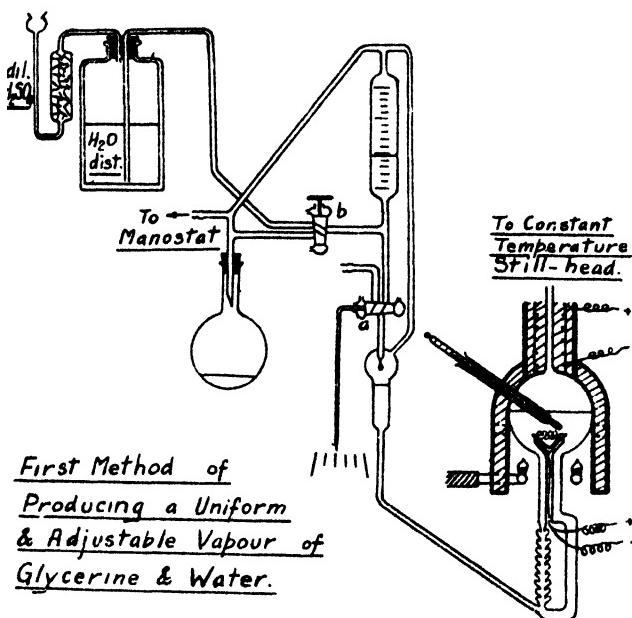


FIG. 1.

sity, the water added by the side tube rises only through the small bulbs and carries with it a nearly equal quantity of glycerin, with which it is almost perfectly mixed by the time the flask is reached. The taps employed were of the mercury sealed type, but glycerin was used both as seal and lubricant. Ordinary rubber tap grease cannot be employed with glycerin solutions. As a considerable amount of ammonia was often present in the laboratory atmosphere, a dilute sulphuric acid trap was used to protect the supply of distilled water.

The second form of still is shown in Fig. 2. In this apparatus the vapour of glycerin and water is produced by passing steam at the temperature of the still through heated glycerin. The steam is produced in the lower flask *b* and is then superheated by passing through a glass tube 18 inches long wound with asbestos-covered resistance wire. The steam then passes through a small bulb (fitted with a sealed-in tube to take a thermo-

meter) and finally through the glycerin to the still head. When allowing the apparatus to cool after finishing an experiment, the long tube inside the flask prevents glycerin passing into the superheater (as this would cause decomposition). To prevent this, air is let into the water flask by tap *d*. By burying the steam flask, superheater and thermometer tube in asbestos wool such a large temperature lag is produced that the voltage variation of the electric power line integrates out and nothing further is required to obtain steam at a practically uniform temperature. To get the best results the steam should be from 8° to 10° above the temperature of the glycerin in order to correct for the cooling effect of glycerin evaporation. The tap *e* is for removing condensed water at the start of an experiment, since otherwise a very long time is required before the thermometer registers correct temperatures. In order to maintain a uniform steam supply, the four holes through which the steam bubbles out are quite small (about 0.4 mm. diameter). This causes a slight back pressure and surface evaporation is sufficient to maintain the steam supply.

**B. The Constant-Temperature Still Head.**—This is shown in Fig. 2. The still head consisted of a resistance glass spiral of 5 turns of 12.5 cms. diameter, the tubing having an internal diameter of 1.5 cms. Before

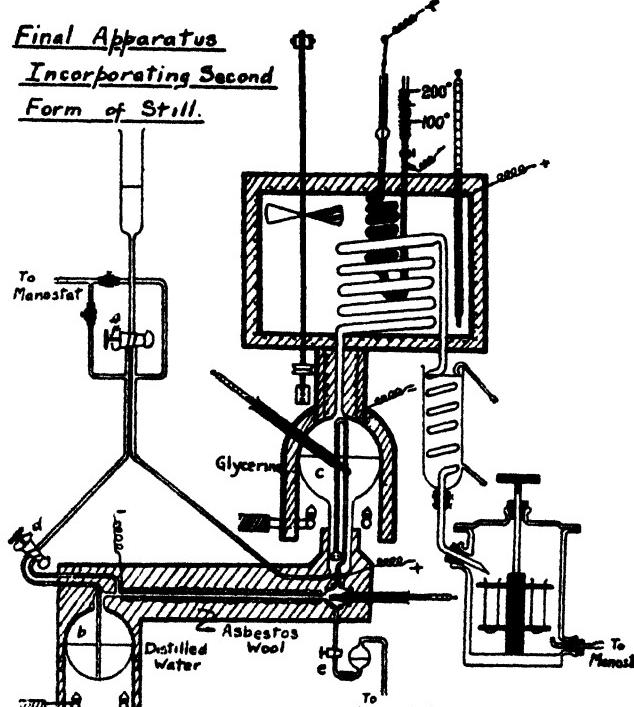


FIG. 2.

adopting this form of still head, many experiments were made with a double-walled copper cylinder, the inside wall of which was covered with a layer of pure tin. Although this still head appears at first sight to be much more suitable on account of its better thermal conductivity, the glass spiral was found to be more efficient. A constant temperature still head is not, properly speaking, a fractionating column, and condensation, if it occurs at all, goes on over its entire surface without re-evaporation. The metal still head had, however, to be definitely abandoned, because it caused excessive decomposition of glycerin and with its use a very considerable amount of supersaturation of the vapour without condensation occurred.

The thermostat enclosing the still head was an electrically heated air-bath stirred by a fan rotating at 5000 revolutions per minute. A mercury thermo-regulator was used, fitted with a Gouy (oscillating) platinum contact.

The temperature variation was not more than  $\pm 0.05^\circ$  C. The current heating the thermostat was also used to heat the tube leading from the glycerin flask to the still head. This tube was surrounded by about 2 inches of asbestos wool, followed by a heating coil and finally by a thick layer of asbestos paper. The thickness of the insulating layer was adjusted

by trial so that the same current would maintain equal temperatures in both the still head and the lead-in tube.

### C. Accessory Apparatus.

The vapour after condensation was collected in a Bruhl

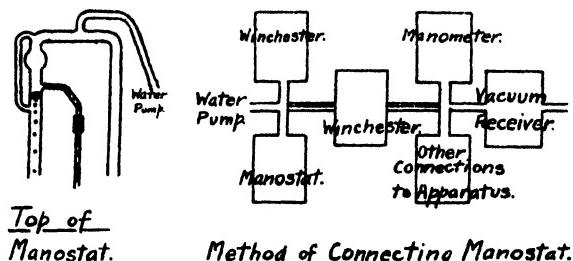


FIG. 3.

vacuum receiver. The pressure regulation was effected by a manostat made after the pattern designed by Wade and Merriman.<sup>1</sup> This was improved by the addition of a small trap at the top, which causes the mercury to collect and fall in a uniform stream. A special gas regulator was devised in order to secure a constant and adjustable flow of gas to the burners.<sup>2</sup> The general arrangement of the accessory apparatus is shown in Fig. 3. The "Winchesters" were used as balancers in order to secure perfectly steady pressures.

### Method of Analysis of Distillates.

For the stronger solutions a Pulfrich refractometer was employed, with a precision of setting equal to  $\pm 0.01\%$ . For the diluter solutions a Rayleigh interferometer (made by Adam Hilger, Ltd.), was used, giving direct comparison between distilled water and glycerin solutions up to 6% strength, with a precision of setting greater than  $\pm 0.001\%$ .

### Calibration of Refractometer and Interferometer.

(a) *Pulfrich Refractometer.*—Dried and purified air was drawn through about 120 g. of glycerin contained in an evacuated litre flask heated to  $45^\circ$  C. After three to four days the glycerin became anhydrous and was weighed in the tared flask after taking the refractive index of a small sample, correction being made for the small amount of moisture absorbed during exposure to the air. From previous experiments at various rates of handling this correction was found to be 0.01% in the sample transferred to the Pulfrich cell and 6 mg. absorbed in the flask. After this point no further correction was necessary for absorption of water. The glycerin in the flask was then diluted with water in successive small stages, the refractive index being determined after each dilution. The samples used in the refractometer were transferred back to the main solution with four washes of distilled water in each case, in order to prevent the accumulation of weighing errors. After the flask became full, part of the solution was discarded and the remainder diluted to 5% strength to overlap with the range of the interferometer measurements.

<sup>1</sup> *J. Chem. Soc.*, 99, 984 (1911).

<sup>2</sup> It is hoped to publish a description of this regulator, which acted with great efficiency.

The flask and its contents were weighed on an Oertling balance sensitive to 1 mg. Before using the flask it was kept under observation for three months, covering almost all weather conditions. In no case did the weight vary by more than 3 mgs. from the mean, if the balance case were opened a minute or so before weighing. On 120 g. of glycerin 3 mg. may be neglected. In order to effect interpolation between the determined points, an equation was found which fitted the points as closely as possible. Differences from this equation (never more than 0.08 %) were then plotted, and a smooth curve through these points constituted a correction curve to values calculated from the equation. The details of this calibration have been given, as a high degree of accuracy is required in the analysis of the glycerin distillates. Since it is thought that the results may be of value to others, the following Table (Table I.) gives the refractive indices of glycerin solutions of known concentrations at 25° C. The values correspond to every 30' in the Pulfrich instrument employed.

TABLE I.—REFRACTIVE INDICES OF AQUEOUS GLYCERIN SOLUTIONS AT 25° C.

$\mu_{D^\circ}$	Per Cent. Glycerin.	$\mu_{D^\circ}$	Per Cent. Glycerin.	$\mu_{D^\circ}$	Per Cent. Glycerin.
1.47352	100.000	2222	66.718	7302	32.210
7312	99.748	1924	64.724	7028	30.166
7016	97.856	1626	62.718	6757	28.122
6719	95.960	1328	60.702	6487	26.080
6421	94.054	1032	58.678	6220	24.038
6123	92.140	0737	56.654	5956	21.996
5824	90.216	0442	54.630	5695	19.954
5525	88.288	0150	52.602	5436	17.916
5225	86.352	139857	50.572	5180	15.880
4925	84.406	9567	48.540	4927	13.850
4624	82.456	9278	46.504	4677	11.824
4324	80.502	8990	44.466	4431	9.814
4022	78.546	8704	42.426	4187	7.814
3722	76.586	8420	40.384	3948	5.832
3422	74.624	8138	38.342	3712	3.866
3122	72.660	7857	36.300	4378	1.912
2822	70.691	7579	34.254	3251	0.000
2522	68.708				

(b) *Interferometer*.—The exact concentration of a solution of glycerin (about 40 %) was determined by means of the Pulfrich Refractometer, a small portion diluted by weight to the strength required (0 to 6%, and compared with distilled water in the interferometer, the process being repeated for the necessary series of concentrations.

### Some Details of Experimental Procedure.

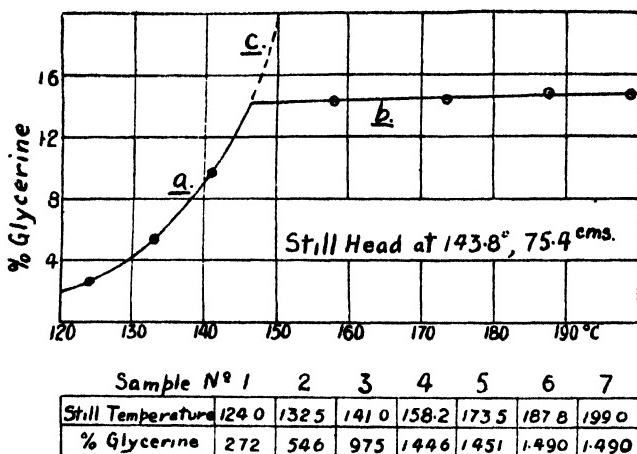
Before measurements can be made, the still head must be dried and freed from glycerin, the glycerin solution must be boiling somewhat below the still head temperature, and the pressure and temperature of the still head must be adjusted to the desired values. In practice the still head was first allowed to remain cool, the condensed vapour washing most of the glycerin in the still head back to the flask. The still head was then heated to the desired temperature and dried by the vapour which was now unsaturated. After a final adjustment of the pressure the conditions were

ready for the measurements to begin, *i.e.* the determination of the glycerin content of the condensed vapour (distillate) as a function of the still temperature (temperature of the glycerin solution in the boiling flask) as this temperature was gradually raised. On plotting these results, a curve and a nearly horizontal straight line are obtained. The point of intersection gives, as already explained, the composition of the equilibrium vapour

corresponding to the pressure and temperature of the still head. An example of a measurement and corresponding plot is given in Fig. 4.

### Experimental Results.

The results obtained are given in Table II. The values represent vapour compositions in equilibrium with liquid at the temperature and pressure of the respective column



*The Effect of Passing Vapour of Glycerine & Water Through a Still Head at Constant Temperature*

FIG. 4.

and row in which they are placed, and are given as weight percentages of glycerin (denoted by  $w$ ). The figures given under  $p$  are partial pressures of glycerin in the vapour (in mm. Hg), calculated on the assumptions that the vapour consists of simple molecules of glycerin and of water and that it obeys Dalton's Law of partial pressures. Despite the utmost care in the individual measurements, four of the results obtained evidently involved some error. These have been discarded and interpolated results (indicated by brackets) inserted in the table. The two final values at 60 mm. pressure (corresponding to 190° and 200°) are also estimated values and are given in brackets.

### The Vapour Pressure of Pure Glycerin.

On examining the results given in Table II., it will be seen that at a constant temperature the partial vapour pressure of glycerin regularly increases as the pressure decreases, *i.e.* as the solution becomes more concentrated with respect to glycerin. A plot of these figures was therefore made, and each series at constant temperature extrapolated to the point where the partial pressure of glycerin becomes equal to the total pressure. At this point one is evidently considering anhydrous glycerin and the value obtained is its vapour pressure at the particular temperature. As the required extrapolation is very small, it is believed that the values found in this way are accurate to about 1%—possibly rather better than this above 170° and a little less accurate below 100°. Some of these plots and extrapolations are shown in Fig. 5.

TABLE II.—VAPOUR COMPOSITIONS AND GLYCERIN PARTIAL PRESSURES.

Temperature.	50°.	60°.	70°.	80°.	90°.	100°.	110°.	120°.	130°.	140°.	150°.	160°.	170°.	180°.	190°.	200°.		
760	w p					0·072	0·236	0·560	1·130	2·135	3·865	(6·74)	10·63	(15·82)	22·98			
						0·1071	0·3517	0·8366	1·696	2·231	5·933	(10·60)	17·29	(26·96)	41·93			
660	w p					0·023	0·107	0·310	0·693	1·380	2·620	4·710	7·81	12·14	18·00	25·91		
						0·0297	0·1383	0·4014	0·9001	1·362	3·456	6·323	10·76	17·39	27·18	42·27		
560	w p					0·047	0·165	0·412	0·863	1·695	3·190	5·635	9·16	14·13	20·84	29·53		
						0·0515	0·1811	0·453	0·9533	1·883	3·588	6·468	10·84	17·58	27·44	42·44		
460	w p					0·012	0·095	0·245	0·552	1·122	2·140	4·020	6·860	11·10	17·00	24·68	34·39	
						0·0108	0·0856	0·2210	0·4991	1·0192	1·960	3·740	6·536	10·98	17·73	27·72	42·79	
360	w p					0·037	0·167	0·352	0·759	1·530	2·890	5·230	8·79	14·12	21·26	30·31	41·06	
						0·0361	0·1178	0·2468	0·598	1·0913	2·084	3·846	6·664	11·22	18·07	28·24	43·19	
260	w p					0·029	0·097	0·272	0·545	1·130	2·180	4·165	7·23	12·19	18·95	27·90	38·63	
						0·0148	0·0494	0·1387	0·2785	0·5802	1·1280	2·193	3·906	6·876	11·376	18·30	28·51	
160	w p					0·025	0·074	0·234	0·543	1·060	2·800	6·75	11·67	19·00	28·41	53·36	66·40	
						0·0078	0·0232	0·0784	0·1708	0·3144	0·6235	1·2973	2·35	4·032	7·022	11·53	29·27	44·62
60	w p					0·014	0·033	0·103	0·285	0·707	1·525	3·160	10·33	17·39	27·36	56·23	70·39	
						0·0016	0·0029	0·0031	0·0035	0·1813	(5·455)	(6·669)	1·3228	2·374	4·119	7·351	12·054	(83·82)
																(94·18)		
																(50·21)		

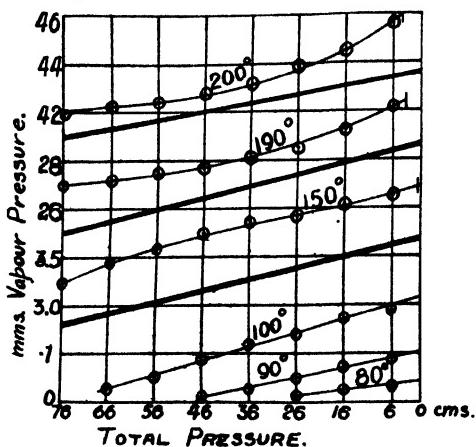
Pressures in mm. Mercury.

The logarithms of the vapour pressures thus determined are shown plotted against temperature in Fig. 6.

The results obtained by Richardson<sup>3</sup> are shown in the same Figure.

### Latent Heat of Evaporation of Glycerin.

The values of the vapour pressure were plotted on a large scale and a curve drawn giving a series of smoothed values. From the latter total latent heats of evaporation were calculated by means of the



Determining Vapour Pressure of Anhydrous Glycerine.

FIG. 5.

simplified Clapeyron-Clausius equation,

$$\text{Log } \frac{\rho_1}{\rho_2} = \frac{L}{R} \cdot \frac{T_1 - T_2}{T_1 T_2}.$$

Table III. gives the "experimental" and "smoothed" values of the vapour pressure ( $\rho$ ) in mm. at the corresponding temperatures.

The irregularity in the calculated values of L is not more than might be expected, considering the very indirect method of calculation and the difficulty of the original measurements. As we should expect, the latent heat falls as the temperature rises.

TABLE III.

Temperature.	200°	190°	180°	170°	160°	150°	140°	130°
$\rho$ (exp.)	46.0	30.3	19.3	12.2	7.55	4.22	2.40	1.35
$\rho$ (smoothed)	46.0	30.3	19.3	12.1	7.4	4.30	2.43	1.35
Temperature.	120°	110°	100°	90°	80°	70°	60°	50°
$\rho$ (exp.)	0.71	0.40	0.215	0.105	0.042	0.017	0.0065	0.0025
$\rho$ (smoothed)	0.74	0.385	0.195	0.093	0.041	0.017	0.0067	0.0025

In Table IV. are given the calculated values of L (in calories per mol.) at the corresponding mean temperatures.

TABLE IV.

Temperature	195°	185°	175°	165°	155°	145°	135°	125°
L	18170	18780	18610	18740	19740	19810	19430	18920
Temperature	115°	105°	95°	85°	75°	65°	55°	
L	19530	19300	19910	20840	21170	21120	21060	

### The Possibility of Systematic Errors in the Method Employed.

Three principal defects might possibly introduce errors: (a) Small particles of spray might be carried over into the distillate. (b) Super-saturation might occur in the still head. (c) A convergence error might occur; equilibrium being only more or less closely approached. To these possible sources of error may be added that due to decomposition of glycerin.

Although the author carried out an extensive series of experiments on these possible errors, the reader may be spared an account of the details. Errors due to (a), (b), and (c) were found to be inappreciable with the form of apparatus employed.

An idea of the amount of decomposition was obtained by a colorimetric estimation of acrolein in the distillates, using a standard sensitive Schiff's reagent. Decomposition of the glycerin may produce an error somewhat larger than that corresponding to the percentage of acrolein found in the distillate. As a rough estimate, it was considered as possibly causing three times this error. With this allowance the error amounted to  $0.024\%$  at  $200^\circ$ , and  $0.006\%$  at  $150^\circ$ , and was undetectable at  $100^\circ\text{ C.}$  (percentage of glycerin content). As regards errors arising from calibration of instruments and precision of reading, the following summarised statement may be made, embracing a careful consideration of all errors of this type:—

*Temperature:  $\pm 0.15^\circ\text{ C.}$*

*Pressure:  $\pm 0.2\text{ mm.}$*

*Analysis by Pulfrich Refractometer:  $\pm 0.016\%$  glycerin.*

*Analysis by Interferometer:  $\pm 0.002\%$  glycerin.*

### Summary.

1. An apparatus has been designed which is capable of measuring the compositions of vapour in equilibrium with aqueous solutions of glycerin.
2. Measurements have been made of the vapour compositions in equilibrium with glycerin solutions from  $50^\circ$  to  $200^\circ\text{ C.}$  and from  $760\text{ mm.}$  to  $60\text{ mm.}$  pressure.
3. The vapour pressure of anhydrous glycerin has been determined from  $50^\circ$  to  $200^\circ\text{ C.}$
4. The latent heat of evaporation of anhydrous glycerin has been calculated from  $55^\circ$  to  $195^\circ\text{ C.}$
5. The accuracy claimed in these measurements is as follows. For vapour compositions, from  $0.1$  to  $0.5\%$  of the glycerin content. For vapour pressures, about  $1\%.$

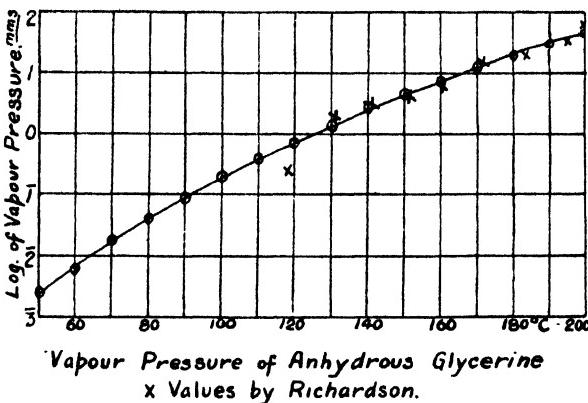


Fig. 6.

In conclusion the author desires to express his best thanks to Professor F. G. Donnan, at whose suggestion this investigation was undertaken, for his kind advice and assistance.

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## THE $P_H$ OF BUFFERED SALT SOLUTIONS.

BY JASPER B. O'SULLIVAN, B.Sc.

*Received 31st January, 1928.*

Haynes<sup>1</sup> has shown that the  $p_H$  of acetate and phosphate buffer solutions is lowered by the addition of certain "neutral salts," including the chlorides of the alkalis, and of barium, calcium, and magnesium. This phenomenon is still more marked in the case of some other metals, as is shown by the following experiments. The author recently had occasion to prepare some nickel sulphate solutions which should retain an approximately constant  $p_H$  during electrolysis. It was, therefore, decided to buffer them, and one of Walpole's acetate buffers was first employed. In the buffered nickel sulphate solution the total acetate concentration was 0·2 molar, whilst the concentration of the nickel sulphate was 0·85 molar. The nickel sulphate without buffer, and the buffer itself both had a  $p_H$  of 5·0, but the  $p_H$  of the mixed solution was found to be 4·4. This lowering of the  $p_H$  of a buffer solution by nickel sulphate was found to be general, as the figures in Table I. demonstrate.

TABLE I.

	1.	2.	3.	4.
$p_H$ of buffer solution . . .	5·0	5·9	6·4	7·1
$p_H$ of ditto with $NiSO_4$ . . .	4·4	5·3	4·5	5·9

Numbers 1 and 2 were acetate buffers, 3 was phosphate 0·05 molar, and 4 was borate 0·2 molar. The  $p_H$  measurements were made with a quinhydrone electrode against a saturated calomel electrode, with saturated potassium chloride as an intermediate.

As the quinhydrone electrode is known to be subject to a salt error in strong salt solutions, it was tested against a hydrogen electrode in nickel sulphate solutions of the above strength, first in the presence of an acetate, buffer, and then in the presence of N/100 sulphuric acid. In neither case, was there an error of more than 0·002 volt, and this error was in such a direction as to give a higher, not a lower  $p_H$ . The quinhydrone electrode was, therefore, employed throughout the subsequent experiments.

The effect of several other salts was next investigated, an acetate buffer of  $p_H$  5·0 being employed in every case. Most of the salts used were commercial "recrystallised" samples, and no attempt was made to purify

<sup>1</sup> *Biochem. J.*, 1921, 15, 440.

them, since there is no reason to suppose that the small quantity of impurity, including free acidity, which might be present would exert any appreciable effect on the  $\rho_H$  of the buffer. The results are summarised in Table II.

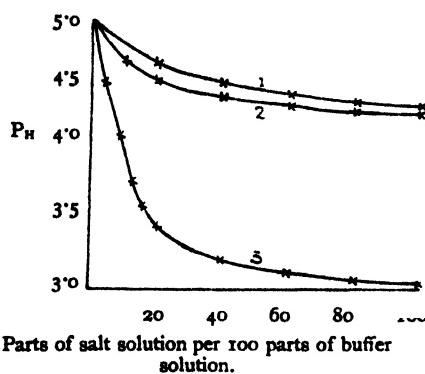
TABLE II.

Added Salt.	$\rho_H$ of 0·8 Equivalent Normal Salt Solution.	$\rho_H$ of same Buffered.	$\rho_H$ of 1·7 Equivalent Normal Salt Solution.	$\rho_H$ of same Buffered.
Barium chloride . . .	4·5	4·8	4·2	4·5
Cadmium chloride . . .	5·7	4·3	—	—
Copper sulphate . . .	3·7	4·0	3·3	3·5
Manganese sulphate . . .	3·9	4·7	—	—
Nickel sulphate . . .	5·0	4·6	5·0	4·4
Aluminium nitrate . . .	3·5	3·1	—	—

The above values for barium chloride are in good agreement with those given by Haynes for an acetate buffer of  $\rho_H$  4·7.

It was thought interesting to investigate a few of the above cases in greater detail, and experiments were, therefore, made with cadmium chloride, nickel sulphate, and aluminium nitrate over a wide range of concentration of these salts, the same buffer being again employed. In order to simplify the technique, the solutions of the salts under investigation were added to separate portions of one buffer solution, which was thereby diluted to a maximum amount of double its original volume. Similar dilution to double volume with water had no appreciable effect on the  $\rho_H$  of the buffer. The results are shown in the accompanying graph, in which the abscissæ represent parts of the salt solution added to one hundred parts of the buffer solution. The cadmium chloride and aluminium nitrate solutions were twice normal, and the nickel sulphate solution was 3·4 normal, since this salt has a smaller effect than either of the others. It will be observed that with cadmium chloride and aluminium nitrate, there is an appreciable lowering of  $\rho_H$  even when the concentration of the added salt is below that of the buffer mixture.

Haynes has shown that the lowering of  $\rho_H$  of a buffer solution by the addition of a salt with no common ion, may be explained on the assumption that new acetates or phosphates are formed by double decomposition with the added salt, and that their electrolytic dissociation is repressed by the excess of the cations of this salt. Further, that the effect should be greater for a salt of a divalent metal than for one of a monovalent metal, owing to the smaller electrolytic dissociation of the acetates and phosphates of the former. Similarly the effect should be still greater for a salt of a trivalent metal; this is supported by the case of aluminium nitrate.



(1) 3·4 N nickel sulphate.

(2) 2 N cadmium chloride.

(3) 2 N aluminium nitrate.

The foregoing experiments were performed during the course of a wider investigation carried out with the aid of a grant from the Department of Scientific and Industrial Research, and it was not, therefore, possible to go into the matter in greater detail. They serve, however, to show the need for checking the  $p_H$  of buffer solutions after the addition of salts.

In conclusion the author wishes to express his thanks to Dr. H. Sand for the interest which he has taken in the above work.

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## THE ACTIVITY COEFFICIENTS OF AQUEOUS SOLUTIONS OF LEAD CHLORIDE AT 25° C.

By A. J. ALLMAND AND E. HUNTER.

*Received 2nd February, 1928.*

In a recent paper<sup>1</sup> outlining an electrometric investigation of the system  $PbCl_2 - KCl - H_2O$  at 25°, it was mentioned that measurements on the cell



had given discordant results. This was particularly the case with the more dilute solutions ( $0.001 M.$  and under) and was ascribed to the action of traces of dissolved air on the lead electrodes. The measurements have now been repeated under air-free conditions, and the results are presented below.

### Experimental.

The cell employed is shown in Fig. 1. A is of about 400 c.c. capacity up to the neck, and is provided with a small well B in its base, a gas inlet-tube C, fused through the side and dipping down into B, and a ground stopper

D. The last is furnished with three short tubular openings E, G, and E', arranged in line, and with a gas exit H. E and E' serve for introduction of the electrodes and G for the stem of a calibrated burette, used to deliver either distilled water or a  $PbCl_2$  solution. The joints are formed by short lengths of pressure tubing, allowing of a close sliding fit.

The chloridised silver electrodes were prepared on 1 cm. squares of platinum gauze, sealed into glass tubing in the usual way. These were silver-plated by deposition from cyanide solution (7 grams  $AgNO_3$  in 100 c.c.  $H_2O$  + 10 grams  $KCN$  in 100 c.c.  $H_2O$ ) for 24 hours, 0.01 amp.

being passed through four such electrodes in parallel. They were then chloridised anodically in 0.1 N.  $HCl$ , 0.028 amp. being passed for thirty minutes through the paralleled electrodes. The lead electrodes consisted of small pear-shaped pieces of Kahlbaum lead fused on to short lengths of

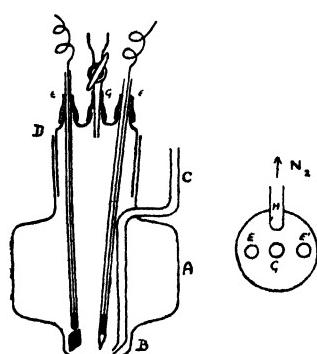


FIG. 1.

<sup>1</sup> Allmand and Burrage, *Trans. Faraday Soc.*, 23, 470 (1927).

platinum wire, fused in their turn into glass tubes. The small exposed lengths of platinum were covered with Baekelite and dried. After cleaning the lead surfaces, these were amalgamated by rubbing in pure mercury. If necessary, the surface was renovated before use by rubbing in filter-paper. The  $\text{PbCl}_2$  (B.D.H.) was of a high degree of purity.

Two cells of this type were placed in a thermostat regulated at  $25^\circ \pm 0.02$ , and their side tubes C connected by short lengths of pressure tubing to the supply of nitrogen used for displacement of air. Their exit tubes H were similarly connected together, the nitrogen finally bubbling out through a water trap. Cylinder nitrogen was used, traces of oxygen being removed by passage over a column of copper turnings kept at  $350^\circ$  to  $400^\circ$  C. in an electric furnace. Before entering the cells, it passed through two bubblers filled with distilled water and kept in the thermostat. Between furnace and thermostat, a side-tube allowed of a stream of the oxygen-free gas being led into the top of a large bottle containing a supply of air-free water. This gas space also connected with the upper ends of the two burettes delivering into the cells; thus, by means of a siphon tube which led, through short lengths of pressure tubing closed by clips, to the bases of the burettes, the operations of filling and emptying the latter could be carried out without admission of air. The distilled water used was freed from air by vigorous boiling and cooled in a nitrogen stream.

We carried out experiments in three different ways: (1) Known weights of a  $\text{PbCl}_2$  solution of known molality (saturated or otherwise) were filled into each of the two cells by calibrated pipettes and, after measurement of the *E.M.F.*, diluted until the cells were full by successive additions of air-free water from the calibrated burettes, the *E.M.F.*'s being measured after each addition. The well at the base of the cell allowed of measurements being made with the original 5 or 10 c.c. added. Five such series were carried out. The initial solutions were as follows:—

*Series A.*—10.091 g. of solution saturated at  $25^\circ$ .

*Series B.*—5.004 " " " "

*Series C.*—10.007 g. of solution containing 0.7947 g.  $\text{PbCl}_2$  per 1000 g.  $\text{H}_2\text{O}$ .

*Series D.*—4.973 " " " "

*Series E.*—57.283 g. of solution saturated at  $25^\circ$ .

(2) To eliminate any possibility of a systematic calibration error, a series (F) of experiments was carried out in which 49.87 g. of water were concentrated by running in from the burettes a solution (of measured density) containing 4.822 g.  $\text{PbCl}_2$  per 1000 g.  $\text{H}_2\text{O}$ .

(3) As a further check, a few experiments were carried out with solutions made up directly by weight.

In all cases, the clean dry cells were first connected up together, the electrodes being slid up through the pressure-tubing connections until well inside the ground-glass stopper, and a stream of pure nitrogen passed through the apparatus for 30 minutes. The burettes were then withdrawn and, after addition of the initial filling, whether water or a  $\text{PbCl}_2$  solution, rapidly replaced. After continuing the gas-stream for a few minutes, the electrodes were lowered into the solution ( $\text{PbCl}_2$  having been added from the burette if the first filling were water), the gas stream stopped, and the *E.M.F.*'s measured. The electrodes were then raised again, fresh water or solution added from the burettes and, after five minutes passage of gas, the electrodes re-lowered and readings taken. In practice, one cell was measured whilst nitrogen was passing through the freshly prepared solution in the other. The potentiometer in use (Cambridge Instrument Company)

permitted of readings being made to 0.0001 volt. Within this limit, the *E.M.F.*'s became very rapidly constant. No attempt was made to dilute (or concentrate) the solutions in the two cells to the same extent. In that sense therefore, the readings of the two cells were not a check on one another. In cases, however, when the two cells contained the same solution, the *E.M.F.* readings agreed to within 0.0002 volt, except once (the initial solution of series C), where the difference was 0.0009 volt.

### Results.

In all, about 220 readings were made, covering the concentration range from saturation down to  $6 \times 10^{-5} M$ . The following remarks may be made regarding the separate series:—

*Series A.*—From saturation to 0.0019  $M$ . Two or three of the *E.M.F.* values in more concentrated solutions somewhat high—good agreement with the mean below 0.01  $M$ .

*Series B.*—From 0.0145 — 0.0009  $M$ . Satisfactory series.

*Series C.*—From 0.0028 — 0.00013  $M$ . One of the cells gave readings for the most dilute solutions consistently lower (about 0.0015 volt) than the mean.

*Series D.*—From 0.0008 — c. 0.0006  $M$ . With one or two exceptions, an excellent series.

*Series E.*—From saturation to 0.01  $M$ . Readings agreeing well amongst themselves, but falling below the mean curve, the deviation increasing progressively with the dilution, and amounting to 0.003 volt at the maximum.

*Series F.*—From 0.013 — 0.001  $M$ . With the exception of four or five adjacent readings in the case of one of the cells, a satisfactory series, coinciding well with the mean curve drawn from the dilution experiments.

The readings given by the solutions made up directly by weight fell satisfactorily on the graph expressing the results. This was drawn out on a large scale, plotting *E.M.F.* against the logarithm of the  $PbCl_2$  molality. There was little difficulty in selecting the best smooth curve to pass through the experimental points. When this was drawn, the only points obviously showing a systematic divergence (see above) were some of the Series C readings in dilute solution, the greater part of Series E, and the small group in Series F—in all, about 30 out of the 220 points. Their causes we imagine to have been in Series C and F, electrode trouble in one of the cells, and, in the case of Series E, an error in making up the original solution, unnoticed at the time but realised later. Their occurrence in no way affects the conclusions which follow.

The graph of the results is shown, purely diagrammatically, with the changes in slope much exaggerated and with a rough indication of the ranges of concentration covered by the different series, in Fig. 2. In the stronger solutions, it is very slightly convex with respect to the origin, shows a point of inflexion somewhere near 0.0007  $M$ , and then becomes slightly

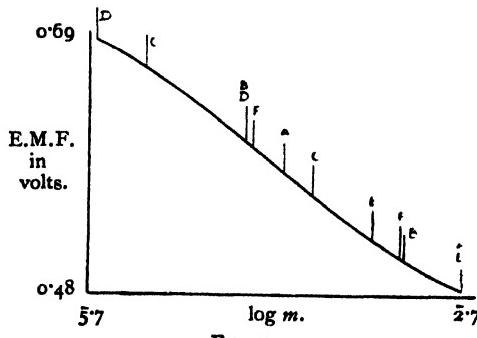


FIG. 2.

concave to the origin. It would be impracticable either to give the experimental results in tabular form or to reproduce in useful manner the large scale experimental graph. We accordingly simply give in Table I. the *E.M.F.*'s. of the cells read off from this curve for a series of round values of  $\log m$ .

TABLE I.

$\log m.$	E (volts).	$\log m.$	E (volts).
2.5920	0.4833	3.2	0.5805
.5	.4881	.1	.5884
.4	.4938	.0	.5963
.3	.4998	.9	.6045
.2	.5063	.8	.6126
.1	.5130	.7	.6208
.0	.5199	.6	.6291
3.9	.5270	.5	.6370
.8	.5345	.4	.6452
.7	.5420	.3	.6532
.6	.5498	.2	.6612
.5	.5574	.1	.6690
.4	.5650	.0	.6762
.3	.5727	.9	.6833

### Discussion.

The shape of the curve as shown in Fig. 2 is readily accounted for. The "convex" portion which starts out from the saturation point corresponds to the gradually increasing value of the activity coefficient ( $\gamma$ ) of the dissolved  $PbCl_2$  with rising dilution, whilst the change over to the "concave" portion is due to the effect of the solubility of  $AgCl$ . If we had not carried our measurements below concentrations of 0.0002  $M$ ., or had done fewer series, we might readily have been led into serious error, as the result of the "silver chloride effect" is to render the curve, for some distance on either side of the point of inflexion, practically linear. A true linearity would of course indicate a constant figure for  $\gamma$ , its value depending on the slope.

Our first attempt at interpretation of the results was based on the treatment applied by Lewis and Randall<sup>2</sup> to analogous measurements carried out by Horsch<sup>3</sup> on  $CdCl_2$  solutions. Using the equation,

$$E = E_0 - \frac{RT}{2F} \ln 4m^3\gamma^3,$$

and making the preliminary assumption that the  $\gamma$  values for  $CdCl_2$  were the same as those for  $BaCl_2$  in solutions of equal molality, they calculated values of  $E_0$  from the various measured values of  $E$ . If the assumption were correct, these calculated values should be identical, and equal to the true  $E_0$ . Over a short concentration range, they did obtain such constancy, within 0.0015 volt. The corrected  $\gamma$  values for the  $CdCl_2$  solutions, recalculated on this basis, indicated that, at concentrations below 0.0004  $M$ , the original assumption was correct, but that, in more concentrated solutions, the  $\gamma$  values rather abruptly became increasingly less than those for  $BaCl_2$ . The figures used for the latter were those calculated by Lewis and Linhart<sup>4</sup>

<sup>2</sup> *Thermodynamics* (1923), pp. 360-361.

<sup>3</sup> *J. Amer. Chem. Soc.*, 41, 1787 (1919).

<sup>4</sup> *Ibid.*, 1951 (1919).

from freezing-point measurements carried out by Hall and Harkins.<sup>5</sup> As Lewis and Randall, in discussing<sup>6</sup> some measurements by Brönsted (see later) similar to our own, came to the conclusion that  $\text{PbCl}_2$  is "nearly as weak a salt" as  $\text{CdCl}_2$ , it seemed that a good starting point in applying the above procedure would be to assume equality between  $\gamma_{\text{PbCl}_2}$  and  $\gamma_{\text{CdCl}_2}$  (taking the Lewis-Randall figures for the latter) in solutions of equal molality, particularly as a plot of Horsch's results on our own experimental curve sheet showed a course nearly parallel to the  $\text{PbCl}_2$  curve over part of the concentration range, deviating at higher concentrations in the direction to be expected if  $\text{CdCl}_2$  were the weaker electrolyte. Table II. contains the results of our calculations, carried out for those concentrations dealt with by Lewis and Randall in the case of  $\text{CdCl}_2$ .

TABLE II.

<i>m.</i>	$\gamma_{\text{CdCl}_2}$	E in Volts	$E'_0$ in Volts	$\gamma_{\text{PbCl}_2}$		
				$E_0 =$ $0.3410 \text{ v.}$	$E_0 =$ $0.3405 \text{ v.}$	$E_0 =$ $0.3400 \text{ v.}$
$0.103 \times 10^{-3}$	0.939	0.6572	0.3370	—	—	—
.109	.938	.6738	.3373	—	—	—
.114	.937	.6721	.3376	—	—	—
.127	.934	.6686	.3381	—	—	—
.153	.930	.6625	.3390	0.979	0.994	0.999
.214	.923	.6507	.3399	0.950	0.967	0.981
2.56	.905	.6349	.3407	.916	.906	.893
.366	.901	.6320	.3409	.903	.891	.879
.479	.872	.6225	.3406	.881	.873	.861
.924	.809	.5991	.3396	.841	.829	.820
2.58	.697	.5639	.3382	.749	.739	.732
3.52	.652	.5537	.3373	.717	.708	.700
7.4	.568	.5294	.3364	.641	.633	.624

The values of  $E'_0$  are seen to change slowly with concentration and to pass through a maximum. This change is a regular one, and shows no signs of any halt over a concentration range. Our preliminary assumption of equality of  $\gamma$  values for  $\text{PbCl}_2$  and  $\text{CdCl}_2$  solutions is thus, up to a point, justified. The occurrence of the maximum  $E'_0$  value means however that, at both lower and higher concentrations than that corresponding to this maximum, the  $\gamma$  values for  $\text{PbCl}_2$  are relatively greater than those for  $\text{CdCl}_2$ . Further, no particular figure can be picked out as being probably the true  $E'_0$ . The last three columns in the table have been calculated on the assumptions that the latter is respectively 0.3410, 0.3405 and 0.3400 volt. The blank spaces for the more dilute solutions correspond to calculated figures greater than unity, and therefore impossible. The reason for these fictitious figures is, of course, the "silver chloride effect" already mentioned. Lewis and Randall<sup>2</sup> estimate this as only affecting the first four concentrations in the table. From the trend of our experimental curve, we imagine that the effect may enter rather earlier, and we prefer not to take into account the first six concentrations, *viz.*, those above the break in the table. Considering the remainder, we see that those in column 5 lie throughout above the figures for  $\gamma_{\text{CdCl}_2}$ . According to Lewis and Randall, however, the  $\gamma$  values of  $\text{BaCl}_2$  and  $\text{CdCl}_2$  are identical for the

<sup>5</sup> *J. Amer. Chem. Soc.*, 38, 2658 (1916).<sup>6</sup> *Thermodynamics* (1923), p. 423.

0.000336 and 0.000366 M. solutions, and it would seem unlikely that  $\gamma_{\text{PbCl}_2}$  would, at any concentration, actually exceed  $\gamma_{\text{BaCl}_2}$ . On the other hand, some doubt would appear to attach to the figures calculated by Lewis and Linhart for  $\text{BaCl}_2$ . They increase abnormally slowly in dilute solutions, and recent values calculated from electrometric measurements by Pearce and Gelbach,<sup>7</sup> whilst agreeing well with those of Lewis and Randall up to 0.01 M., are considerably higher over the rather short range of less concentrated solutions covered by them. If Lewis and Linhart's figures are indeed too low, then the objection to putting  $E_0 = 0.3410$  volt would disappear.

With regard to columns 6 and 7 in the table, it will be seen that, at one or more concentrations,  $\gamma_{\text{PbCl}_2}$  is less than  $\gamma_{\text{CdCl}_2}$ , i.e. it appears as a weaker electrolyte than the latter. It must, however, be noted that, over this concentration range,  $\gamma_{\text{CdCl}_2}$ , as calculated by Lewis and Randall, appears to change at an abnormally rapid rate, this being immediately succeeded by the slow rate ascribed to it in common with  $\text{BaCl}_2$ .

A further attempt was made to evaluate  $E_0$  with more certainty by plotting  $\log \gamma + k = \frac{E_s - E}{0.08872} - \log 4m^{\frac{1}{2}}$  against some suitable power of  $m^8$ . The intercept of the extrapolated curve on the  $\log \gamma + k$  axis ( $m = 0, \gamma = 1$ ) gives the value of  $k$ , which, in its turn, is equal to

$$-\log 4^{1/3} m_s \gamma_s = \frac{E_s - E_0}{0.08872}.$$

The  $E$  and  $m$  values used were those contained in Table I. Plots were made of the  $\log \gamma + k$  function against  $m^{1/2}$  and  $m^{2/3}$ . Owing to the "silver chloride effect," the last six points on the graph could not be used for extrapolation, which makes the results less certain than we could wish. The best value of  $k$  we take as 1.62—it may perhaps be higher, but will not exceed 1.63, and is unlikely to be lower. Table III. contains figures for  $E_0$  and  $\gamma_s$  calculated from these values of  $k$ , and also figures for  $\gamma_s$  and  $k$  calculated from the  $E_0$  values contained in Table II.

The last two values of  $k$  would be outside the limits of error of our extrapolations, and we prefer to base our calculations on  $k = 1.62$ . Table IV. contains our final data for round concentrations, calculated from  $E_0 = 0.3396$  volt, together with data of other workers for  $\text{PbCl}_2$ ,  $\text{BaCl}_2$  and  $\text{CdCl}_2$ .<sup>8</sup>

The  $\gamma_{\text{PbCl}_2}$  figures calculated by Lewis and Randall are based on measurements made by Brönsted<sup>10</sup> over a wide range of temperatures on the cell 0.72 %.

Pb amalgam | Aqueous  $\text{PbCl}_2$  | AgCl (solid) | Ag.

<sup>7</sup> *J. physical Chem.*, 29, 1023 (1925).

<sup>8</sup> The suffix  $s$  refers to a solution saturated with  $\text{PbCl}_2$ , whilst 0.08872 is  $2.303 \times \frac{3RT}{2F}$ .

<sup>9</sup> The values due to Getman are taken from a paper which appeared after our work had been written up. (*J. physical Chem.*, January, 1928.)

<sup>10</sup> *Z. physikal. Chem.*, 56, 645 (1906).

TABLE III.

$k$	$E_0$	$\gamma_s$
1.63	0.3387	0.3776
1.62	0.3396	0.3864
1.615	0.3400	0.3908
1.610	0.3405	0.3954
1.604	0.3410	0.4009

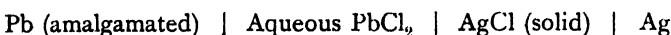
TABLE IV.

<i>m.</i>	E in Volts.	$\gamma$	$\gamma$ (L. and R.)	$\gamma_{\text{CdCl}_2}$		$\gamma_{\text{BaCl}_2}$	
				L. and R.	Getman.	L. and L.	P. and G.
0·03908 (saturated)	0·4833	0·388	0·39	—	—	—	—
·03	·4893	·431	—	—	0·40	—	0·619
·02	·4998	·494	0·47	0·44	0·49	0·655	0·65
·01	·5200	·584	0·55	0·532	0·64	0·716	0·716
·005	·5420	·660	0·63	0·61	0·76	0·771	0·808
·003	·5590	·707	—	0·67	0·83	0·805	0·850
·002	·5726	·745	0·74	0·71	0·86	0·830	—
·001	·5964	·802	0·81	0·805	0·89	0·865	—
·0005	·6210	·848	—	0·87	—	0·894	—
·0003	·6390	·886	—	0·91	—	0·91	—

As only three concentrations of  $\text{PbCl}_2$  were used by Brönsted, the agreement with their results is satisfactory. For reasons already stated, we think that their figures for  $\gamma_{\text{CdCl}_2}$  and  $\gamma_{\text{BaCl}_2}$  in the more dilute solutions may be, respectively, too high and too low. Getman's recent and still higher figures for  $\gamma_{\text{CdCl}_2}$  would point to this salt being a stronger electrolyte than  $\text{PbCl}_2$  at all concentrations below 0·02 M.

### Summary.

(1) Measurements have been carried out at 25° C. on the element,



between the concentration limits of saturation and 0·00006 molar.

(2) From the results, the mean activity coefficients of the dissolved lead chloride have been calculated between the concentration limits of saturation and 0·0003 molar.

(3) The agreement with Lewis and Randall's deductions from Brönsted's earlier measurements is very fair. Reasons are given for thinking that their values for the activity coefficients of barium and cadmium chloride solutions may need revision.

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### REVIEWS OF BOOKS.

**Chemical Encyclopaedia. An Epitomized Digest of Chemistry, and its Industrial Applications.** By C. T. KINGZETT, F.I.C. Fourth Edition. (London, 1928 : Baillière, Tindal & Cox. Pp. ix and 807. Price 35s. net.).

One is tempted to speak of the declining years of most men who can look back over more than fifty years of strenuous industrial life, but the author's virility is displayed by the production in less than ten years of four editions, each more complete than the last, of his labour of love.

The first edition of this work appeared under the title "Popular Chemical Dictionary" shortly after the war. The present title was adopted in the third edition in order to dispel a possible impression that the work is not strictly scientific in nature and in accuracy. The volume purports to be of service

not only to those engaged in the profession and industry of chemistry, but also to the many laymen who are increasingly brought into touch with its multifarious ramifications.

For the layman the language is as simple as the subject warrants and the style clear and concise. For the chemist the book is equally serviceable; there is no other volume comprising such a mass of useful information, and moreover each article contains adequate references to the literature when more detailed study is required.

The volume is excellently printed and adequately bound.

**The Phase Rule and its Applications.** By A. FINDLAY, M.A., D.Sc. Sixth Edition. (Text-books of Physical Chemistry. Longmans, Green & Co. 1927. Pp. xv. and 326. Price 10s. 6d. net)

The appearance of this twenty-three-year-old work in its sixth edition speaks for itself. *Plus ça change, plus c'est la même chose*, and although there are considerable and important changes to record in this latest edition, we who have been nurtured on older editions of the book realise that its philosophical outlook remains in essence unchanged.

To descend to detail, the most important part of the book—that which deals with systems of one and of two components—has been very completely recast, room being made for a discussion of Smit's theory of allotropy, and of equilibria in intensively dried systems. A new chapter has been added dealing with practical applications of equilibrium diagrams.

Although much more extended use is made in this edition of the equation,

$$\frac{dp}{d\theta} = \frac{a}{\theta(V - v)},$$

in discussing the variation of equilibria with pressure and temperature, the use of complex mathematical ideas is consistently avoided, and the work still holds its place as one of the best extant non-mathematical expositions of the Phase Rule.

A. F.

**Chemical Affinity.** By L. J. HUDLESTON, M.C., B.Sc., A.I.C. Monographs on Inorganic and Physical Chemistry. Edited by Alexander Findlay. (London : Longmans, Green & Co. Pp. vii + 135. Price .)

Mr. Hudleston's book is really an elementary introduction to thermodynamics and its applications to chemistry, although what he calls the "forbidding name" of thermodynamics is disguised by the rather vague and unsatisfactory expression "chemical affinity." The subject, he says: "has passed through three stages of development. Willard Gibbs laid the fundamental mathematical foundation, the van't Hoff-Nernst school showed how this may be applied to chemical problems on the basis of general, approximate laws, and G. N. Lewis, by the happy introduction of the term 'activity,' retained these general equations in all their original simplicity, and yet showed how to make them applicable with precision to each specific case." Accordingly, the author gives a simplified and abridged account of the subject on the lines of Lewis and Randall's "Thermodynamics," the nomenclature and numerical data of which he closely follows. His book will, therefore, serve as an introduction to Lewis and Randall's for the weaker students, although the larger treatise is so clearly written that it may be doubted whether this will ever really be necessary.

Mr. Hudleston makes the usual mistake of unwary writers on page 23, when he integrates the adiabatic equation of an ideal gas on the assumption that  $\gamma$  is a

constant, and it is unfortunate that he makes this the basis of his deduction of the equation of the Second Law. Although he quotes on page 54 a source from which "a clear account of the mathematics of partial differentiation" may be obtained, he uses on that page an incorrect notation which teachers find it difficult sometimes to prevent students from using.

It is not until page 102 in this book of 128 pages that the subject which the title leads one to expect is reached. As the author says in his preface, "the term 'monograph' usually implies a detailed and comprehensive exposition of some very limited field for the benefit of advanced students." Such a treatment, on the lines of Sackur's and Pollitzer's books, brought up to date and with a treatment of really interesting and important problems such as the synthesis of methanol, hydrogenation, the water-gas equilibrium, etc., would have been most useful, and it is much to be regretted that the author and editor have missed such a good opportunity. In itself, apart from a few weak spots, the book is well written and accurate, and it will without doubt be found useful. It is not, however, a monograph on "Chemical Affinity."

J. R. P.

**Kurzer Leitfaden der Photochemie im Dienste der Medizin.** By J. PLOTNIKOW. (O. Thieme, Leipzig. Pp. 186.)

Of recent years the effect of radiation as physiological and psychological factors in health has gradually attained the recognition which it undoubtedly deserves. Whilst the physiological effects are undoubtedly due to photochemical reactions, it must be admitted that up to the present their very complexity has been a hindrance to their elucidation. It is thus very appropriate whilst the attention of the medical world is being focussed on photochemistry that Professor Plotnikow, one of the pioneers in this difficult field, should have produced this little volume. As a descriptive account of the general effects of radiation including both the chemical, electrochemical, as well as the mechanical effects exemplified in photophoresis, the book is both interesting and stimulative to thought. If, however, we seek for an expression of the present developments on the effects of interaction of radiation and molecules, it must be admitted that but few people would find themselves in sympathy with Professor Plotnikow's point of view. To give only two instances of this divergence of opinion we might mention the treatment of the Stark-Einstein law of photochemical excitation; this law is now generally accepted as one of fundamental importance, yet we find on page 56 that not only is the "law" misinterpreted, but the whole concept is considered as fundamentally unsound. Again in Chapter VII. the influence of temperature on photochemical reactions is surveyed. The author apparently still adheres to his view that photochemical reactions can be classified into groups, those possessing temperature coefficients of  $1.03 \pm 0.03$ ,  $1.20 \pm 0.03$ , and  $1.40 \pm 0.03$  respectively. A critical examination of the experimental data leads to the conclusion that this apparent regularity is purely fortuitous.

In addition many points of fundamental importance to modern photochemistry are omitted; we find, for example, scarcely any treatment of the properties of excited or active molecules and atoms or of the various alternative suggested mechanisms of dissociation for homopolar diatomic molecules.

In spite of these criticisms there is much of interest in the book in which the ideas are developed both clearly and in an interesting manner.

E. K. R.

# THE KINETICS OF THE HYDROLYSIS OF CERTAIN GLUCOSIDES (SALICIN, ARBUTIN AND PHLORIDZIN).

BY EMYR ALUN MOELWYN-HUGHES.\*

(Received 6th February, and read 29th February, 1928.)

Numerous publications are available dealing with the hydrolysis of glucosides<sup>1</sup> by means of enzymes, notably emulsin and maltase. Relatively little, however, has been published with reference to the hydrolysis of glucosides by means of acids, and only in the case of amygdalin<sup>2</sup> has the temperature coefficient of the reaction been given. Salicin, arbutin and phloridzin are hydrolysed by dilute mineral acids at moderately high temperatures into glucose and salicyl alcohol, glucose and quinol, glucose and phloretin respectively. A slight difficulty in the polarimetric examination of each of these glucosides is due to the behaviour of the aromatic compound which is liberated during hydrolysis. Thus, salicyl alcohol produces an emulsion, quinol imparts a colour to the solution, and phloretin is insoluble. Salicin was chosen for examination in the first instance on account of its ease of purification, and the comparative simplicity of its molecular structure.<sup>3</sup>

## The Hydrolysis of Salicin.

Noyes and Hall<sup>4</sup> find that salicin is hydrolysed at 95° in the presence of acids according to the same law as that which governs the inversion of cane sugar. The above authors establish a direct proportionality between rotatory power and the quantity of salicin present in solution. Noyes and Hall introduce a term "c," which they define as the ratio between the rotations of a 5 per cent. solution of salicin before and after hydrolysis. The numerical value given by them for this factor at 95° C. is 0·487. The value found by the writer to hold at 60° C. is 0·483. This is important in that it indicates that the total rotational change which accompanies the hydrolysis of a given weight of salicin is almost independent of the temperature at which the hydrolysis is carried out. Finally, the above authors employ the term "c" to calculate the initial rotation of the reaction mixture. The value given by them is almost identical with the value which the writer has determined, using a method of graphical extrapolation due to Rosanoff.<sup>5</sup>

*The Purity of Salicin.*—The values for the specific rotation at 25° C.

\* Communicated by Professor W. C. M. Lewis.

<sup>1</sup> The term *glucoside* is used throughout in its restricted sense, i.e. to denote any compound one of the products of hydrolysis of which is glucose.

<sup>2</sup> Caldwell and Courtauld, *Trans. Chem. Soc.*, 91, 666 (1907).

<sup>3</sup> Cf. Irvine and Rose, *Trans. Chem. Soc.*, 89, 814 (1906).

<sup>4</sup> *Z. physikal. Chem.*, 18, 240 (1895).

<sup>5</sup> *J. Amer. Chem. Soc.*, 33, 1911 (1911).

and for the melting-point of the salicin employed are given below, along with some of the values given by other workers:—

TABLE I.

Authority.	Specific Rotation.	Melting-Point.
Thorpe ( <i>Dict. of Appld. Chem.</i> ) . . .	- 65°	201° C.
Clarke ( <i>Organic Analysis</i> ) . . .	- 62.5°	201° C.
Noyes and Hall <sup>4</sup> . . .	- 62.2°	-
Moelwyn-Hughes . . .	- 62.25°	200°-201° C.

Samples of salicin supplied by Kahlbaum and by B. D. H. have been found to be equally pure. The melting-point recorded is a corrected value.

*The Solubility of Salicin.*—In order to know the upper limit to the concentration of salicin that could be employed, the solubility of the glucoside had to be determined. This was done by comparing the above value of the specific rotation with the rotation of a 1/5 saturated solution. The saturated solution was prepared by agitating in a thermostat for several days a vessel containing distilled water with excess salicin. After filtration in the thermostat at 25° C., the solution was diluted to five times its volume, and the rotation of this solution was measured in a polarimeter, the tube of which was kept at 25° C. The value obtained for the solubility of salicin at this temperature is 4.49 g. per 100 c.c. of solution, a value somewhat higher than that given in Seidell's Table of Solubilities, which is 4.16 g. per 100 g. of water. In the same way, the solubilities of amygdalin and arbutin have been determined polarimetrically. The values are:—

TABLE II.

Glucoside.					Solubility in g. per 100 c.c. of Solution at 25° C.
Salicin	.	.	.	.	4.49
Arbutin	.	.	.	.	14.90
Amygdalin	.	.	.	.	11.83

As far as can be ascertained, the last two have not been previously determined.

*Outline of Experimental Procedure.*—Piria<sup>6</sup> and Kraut<sup>7</sup> have shown that the hydrolysis of salicin consists of the following two reactions:—

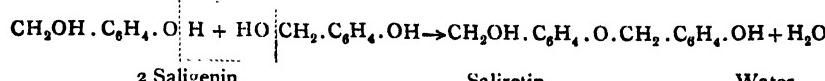


and

615

61-81

10



The latter reaction is stated to be by far the more rapid, hence any measurements of the rate of hydrolysis of salicin will refer only to the first reaction, which, moreover, is the only one which can be followed polarimetrically.

<sup>6</sup> *Annales Chim. Phys.*, 257 (1845).

7 *Ausgaben* 06. 133 (1870)

metrically. When a 5 per cent. solution of salicin is hydrolysed by normal HCl in a polarimeter tube which is kept at 60° C., rotational readings can be taken during the first hour only. The reaction mixture, after removal from the tube, exhibits an opacity which persists after many filtrations. Filtering through charcoal lessens the turbidity. The filtered solution is translucent to white light but perfectly opaque to sodium light. The cloudiness developed during the reaction is probably due to the formation of an emulsion of saliretin in water. This renders the ordinary way of following the reaction useless. It is obvious that, before polarimetric measurements can be taken, the reaction mixture must be freed from saliretin. The process which brings this about must also bring about a "chilling" of the reaction. Further, the method adopted for removing the saliretin and for stopping the reaction must be one which does not in any way alter the rotatory power of the reaction mixture.

Piria<sup>6</sup> stopped the reaction by pouring the cloudy liquid into a saturated solution of lime. It was found that this method satisfactorily removed the saliretin, and stopped the reaction within about two minutes, due to the joint effects of cooling (due to mixing) and the partial neutralisation of the acid present in the reaction mixture. The substitution of CaCO<sub>3</sub> (pulverised calcite) for lime permitted a greater degree of reproducibility of results. The accuracy of the method is dependent on the ratio of the volume of reaction mixture removed to the volume of CaCO<sub>3</sub> solution employed. When this ratio is small, the reaction is stopped almost immediately; experiment showed that the most satisfactory value for this ratio is 2 : 3. The rotations given in Table IV. are those which would be obtained for the reaction mixture before the process of dilution, and are derived by multiplying the observed rotation by the ratio of the final volume examined and the volume actually removed from the reaction vessel. It has been found advisable to do this in order to arrive at uniformity for the purposes of comparison. The readings given in each table are those which would be found if the reaction could be followed in the polarimeter tube in the ordinary manner as in the case of sugar hydrolysis.

25 g. of dry salicin are weighed into a 500 c.c. stoppered flask, 300 c.c. of distilled water are added, and the vessel placed in a thermostat regulated at 60° C. At the requisite instant, 125 c.c. of 4*N*. HCl are added at 60° C. The volume of the mixture is brought up to the mark by the addition of distilled water at 60° C. The vessel is removed from the bath and vigorously shaken. The mean time of removal of the reaction vessel and its return is taken as zero time. Samples (20 c.c.) of the reaction mixture are removed periodically, and are run into flasks containing 30 c.c. of water and about 3 g. of CaCO<sub>3</sub>. Each flask is shaken until effervescence ceases (this being essential in order to coagulate the saliretin emulsion completely), and is cooled to 0° C. in ice. Finally, the sample is filtered, and since the filtered solution is at equilibrium, polarimetric readings may be taken at any convenient time. The infinity reading is found by following the reaction in this way until no further change in rotation is observed; samples removed during the sixth and seventh days were found to have the same rotation. The zero reading is found according to Rosanoff's method.<sup>5</sup>

*Sources of Error.*—The accuracy of the experimental method outlined above depends on the efficiency of the chilling process. The first column of Table III. contains the rotations of various solutions of reaction mixtures containing salicin, the rotations being those taken immediately after chilling. The rotations in the third column are those taken of the same solutions after the specified length of time. The chilling process is quite effective.

TABLE III.

Immediate Rotation.	Time Interval.	Final Rotation.
- 4°39°	2 days	- 4°40°
- 4°39°	5 "	- 4°49°
4°25°	38 "	4°30°
74°22°	34 "	74° or *

Other sources of error involved in the method arise out of the possible changes in volume of a sample of the solution that is examined. Changes in volume may be due to : (1) Contraction on cooling from 60° C. to 20° C. This change in volume will introduce an error of 0·56 % in the rotation. (2) The removal of precipitated saliretin from the solution introduces an error of the same magnitude, i.e. 0·60 %—a value which has been calculated from the assumption that the density of saliretin is 1·5 g./c.c. This body floats in chromic acid and sinks in water. (3) The error due to the removal from the solution of the stoichiometric quantity of water which disappears during hydrolysis is minute, and is moreover partly counterbalanced by the production of half this amount of water during the condensation of two molecules of saligenin to form one molecule of saliretin. The error is 0·06 %. From these considerations, it will be seen that the rotational readings of the solutions examined are liable to an error of not more than 1·5 %.

It may be noted that the phenomenon of muta-rotation does not enter into the problem. It can be justifiably inferred from the results of Hudson and Paine<sup>8</sup> that the change due to muta-rotation in the presence of normal HCl at 60° C. will be immeasurably rapid. Furthermore, Armstrong<sup>9</sup> has demonstrated that salicin is a  $\beta$ -glucoside; the glucose produced during hydrolysis is  $\beta$ -glucose, a modification which has been shown by Colin and Chaud<sup>10</sup> to exhibit a low positive rotation.

*The Velocity-constant Equation Employed.*—The fundamental assumption underlying all polarimetric measurements of chemical reactions is that the rotational change is a direct measure of chemical change—an assumption which receives ample support from the specifically directed investigations of Ostwald<sup>11</sup> and of Rosanoff<sup>6</sup> as well as from the general success to which its adoption has led. No direct proportionality has hitherto been established between the optical rotation of a solution containing glucose plus *glucoside* and the percentage of glucoside present. With this end in view, synthetic mixtures were prepared containing varying amounts of glucose and salicin, and the rotation of each mixture was taken at room temperatures. It was found that the observed rotation in each case agreed well with that calculated from the mixture-law equation:—

$$a = \frac{1}{\sqrt{2}}g \{a_1g_1 + a_2g_2\}$$

in which  $a_1$  = specific rotation of glucose in normal HCl.

$a_2 = \dots$  salicin

$g_1$  = grams of glucose per 100 c.c. of solution.

$\text{g}_1$  = grams of glucose  
 $\text{g}_2$  = " salicin

and  $\frac{g_2}{\frac{1}{8}} =$  the ratio of the length of the polarimeter tube (4 dm.) and the volume of solution (100 c.c.) containing  $g$  grams of solute.

<sup>8</sup> *J. Amer. Chem. Soc.*, **31**, 1242 (1909).

<sup>9</sup> Proc. Roy. Soc., 76B. 592 (1905).  
<sup>11</sup> J. prakt. Chem., 29, 390 (1884).

It must be emphasised that direct proportionality between the rotation of the solution and the percentage of salicin present has been established at room temperatures, when it is known that the solution contains glucose and salicin *only*. At higher temperatures, however, the solution is known to contain some di-glucose,<sup>12</sup> and the mixture law is no longer applicable. It has been shown, in confirmation of earlier workers, that glucose undergoes partial condensation under the conditions of the above experiments. When only 5 % solutions of salicin are hydrolysed at 60° C. and 70° C., the percentage of di-glucose present is minute, hence the ordinary form of the equation for calculating the unimolecular constant is applicable to such dilute solutions of salicin. The equation employed is :—

$$k = \frac{2.303}{t} \log_{10} \frac{a_\infty - a_t}{a_\infty - a_0}$$

in which

$t$  = time, in seconds,

$a_0$  = observed initial optical rotation,

$a_\infty$  = " infinity " "

$a_t$  = " optical rotation after time  $t$  seconds.

*Experimental Results* :—Table IV. gives the values of the unimolecular velocity constant governing the hydrolysis of 5 % salicin by means of normal HCl at 60° C. and 70° C. respectively. By substituting these values for the velocity constants in the Marcelin-Rice equation, the critical increment of the reaction is found to be 31,900 calories.

TABLE IV.—VELOCITY CONSTANTS FOR THE HYDROLYSIS OF 5 % SALICIN BY N. HCl.

Time (Minutes).	Rotation (Degrees).	$k \times 10^5$ (Seconds <sup>-1</sup> ).	Time (Minutes).	Rotation (Degrees).	$k \times 10^5$ (Seconds <sup>-1</sup> ).
		At 60° C.			At 60° C.
0	- 12.60	—	0	- 12.59	—
25	- 12.16	1.57	180	- 9.53	1.64
125	- 10.57	1.52	300	- 7.73	1.65
1190	+ 0.40	1.64	360	- 6.90	1.66
1271	0.90	1.64	420	- 6.12	1.67
1500	2.08	1.67	555	- 4.60	1.65
1610	2.42	1.64	600	- 4.12	1.65
2900	5.11	1.59	1470	+ 1.91	1.65
—	—	—	2920	5.34	1.59
Inf.	6.30	—	Inf.	6.31	—
	Mean = 1.61			Mean = 1.61	
		At 70° C.			At 70° C.
0	- 12.86	—	0	- 13.27	—
15	- 11.73	6.76	70	- 8.53	6.63
70	- 8.40	6.32	135	- 5.15	6.65
210	- 2.05	6.61	225	- 1.75	6.62
270	- 0.28	6.61	297	+ 0.20	6.59
330	+ 1.10	6.60	375	1.65	6.44
420	2.48	6.42	440	2.93	6.73
600	4.65	6.84	—	—	—
Inf.	6.28	—	Inf.	6.23	—
	Mean = 6.59			Mean = 6.61	

Average value of  $k$  at 60° C. =  $1.63 \times 10^{-5}$  (Seconds<sup>-1</sup>).

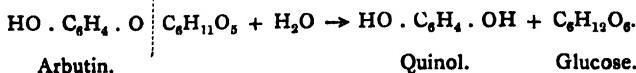
	At 70° C.			At 70° C.
0	- 12.86	—	0	- 13.27
15	- 11.73	6.76	70	- 8.53
70	- 8.40	6.32	135	- 5.15
210	- 2.05	6.61	225	- 1.75
270	- 0.28	6.61	297	+ 0.20
330	+ 1.10	6.60	375	1.65
420	2.48	6.42	440	2.93
600	4.65	6.84	—	—
Inf.	6.28	—	Inf.	6.23
	Mean = 6.59			Mean = 6.61

Average value of  $k$  at 70° C. =  $6.60 \times 10^{-5}$  (Seconds<sup>-1</sup>).

<sup>12</sup> Cf. Moelwyn-Hughes, "The Reactivity of Glucose in the presence of HCl," see p. 321.

## The Hydrolysis of Arbutin.

Arbutin was shown by Strecker<sup>13</sup> to be a glucoside of quinol. It is hydrolysed by acids according to the following equation:—



Its rotatory power and its behaviour towards emulsin classify it as a  $\beta$ -glucoside. Macbeth and Mackay<sup>14</sup> find that completely methylated arbutin gives on hydrolysis the butylene-oxide variety of tetramethylglucose, a result which is analogous to that arrived at by Irvine and Rose<sup>3</sup> in the case of salicin.

*The Purity of Arbutin*.—As in the case of salicin, the two criteria of purity employed were specific rotation and the melting-point. The arbutin employed, which was supplied by Kahlbaum, possessed a specific rotation of  $-62.26^\circ$  (mean of two results agreeing within  $0.03^\circ$ ). It will be seen from Table V. that this is intermediate between two of the values which have been found in the literature, and from Table I. that the specific rotations of salicin and arbutin are equal.

TABLE V.

Authority.	Specific Rotation Arbutin at 25° C.
Ullmann ( <i>Enzyklopädie der technischen Chemie</i> )	- 60° 34°
Thorpe ( <i>Dictionary of Applied Chemistry</i> )	- 63° 50°
Moelwyn-Hughes (measured in water)	- 62° 26°
(measured in normal HCl)	- 63° 13°

It is of interest to note that the specific rotation is greater when the measurement is carried out in normal HCl instead of in water. Vosburgh<sup>15</sup> states that the presence of deci-normal HCl does not affect the value of the specific rotation. Table VI., however, demonstrates that the specific rotations of glucose, salicin, and arbutin measured in normal HCl are about 1 % greater than the corresponding values for pure aqueous solutions.

TABLE VI.

Optically Active Solute.	Specific Rotation at 20° C. or 25° C.	
	Measured in Water.	Measured in Normal HCl
Glucose	+ 52·47	+ 52·90
Salicin	- 62·25	- 62·81
Arbutin	- 62·26	- 63·13

The arbutin employed resembles many of the sugar derivatives in possessing two melting-points. When immersed in a bath previously heated to 170° C., the substance instantly melts. On cooling, freezing sets in at 165° C.; subsequent heating results in a melting-point at 194° C. These values are in agreement with those given by Clarke and by Herissey.<sup>16</sup> Three experiments carried out by the Pregl-Zeisel micro-analytic method

<sup>13</sup> *Annalen*, 107, 231 (1858).

<sup>15</sup> *J. Amer. Chem. Soc.*, **43**, 1693 (1921).

<sup>14</sup> *Trans. Chem. Soc.*, 123, 717 (1923).

<sup>16</sup> Comp. Rend., 151, 444 (1910).

for the determination of alkyl groups indicated that the arbutin employed contained less than 0·5 % of  $-OCH_3$ , and is, therefore, practically free from methyl-arbutin.<sup>17</sup>

*The Total Rotational Change.*—The total rotational change which accompanies the hydrolysis of a known mass of arbutin has been determined directly, by measuring the initial and final rotations of solutions at room temperatures. The results of three experiments give a mean value of  $+3\cdot85^\circ$  for the increase in positive rotation associated with the hydrolysis of unit mass of arbutin (Table VII.). The value calculated from the specific rotations of arbutin and glucose (in normal HCl) is  $+3\cdot79^\circ$ .

TABLE VII.

Grams of Arbutin/100 c.c.	Initial Rotation.	Infinity Rotation.	Change in Rotation Per Gram Arbutin.
1·806	$-4\cdot63^\circ$	$+2\cdot40^\circ$	$+3\cdot89^\circ$
3·192	$-8\cdot08^\circ$	$+4\cdot16^\circ$	$+3\cdot83^\circ$
3·850	$-9\cdot70^\circ$	$+5\cdot02^\circ$	$+3\cdot82^\circ$
Mean = $+3\cdot85$			

### Experimental Procedure and Results.

The solution examined in each case contains 10 g. of arbutin in 100 c.c. of volume-normal HCl, and is prepared exactly as in the case of salicin; 25 c.c. of the reaction mixture are rapidly removed into a 4 dm. polarimeter tube which has been previously heated to the requisite temperature. An intense sodium flame was employed as the source of illumination. A slight experimental difficulty in measuring rotations is due to the production of a deep red colour in the solution, which, after 10 hours at 60° C., will not transmit sufficient light to render the polarimetric reading accurate. It is therefore fortunate that the hydrolysis is more than 75 % complete at this time.

That the production of colour referred to above is due to the atmospheric oxidation of quinol has been rendered probable by the following observation. On previously saturating the experimental solution with CO<sub>2</sub> the intensity of colour (estimated in the colorimeter) is reduced by about 12 % of its original value. Armstrong,<sup>18</sup> who observed the same phenomenon during an investigation of the action of enzymes on arbutin, attributed the colour to the catalytic oxidation of quinol *by means of oxidase*. In view of the instability of oxidase at 60° C. and 70° C.,<sup>19</sup> and the fact that it displays optimum catalytic activity at  $p_H = 7 - 10$ ,<sup>20</sup> it appears highly improbable that oxidase can exist at all under the conditions of the present experiments, *i.e.*, in the presence of normal acid at 60° C. and 70° C. The explanation given by Armstrong is thus seen to be untenable.

Table VIII. below gives the values of the unimolecular constants governing the hydrolysis of 10 per cent. arbutin by means of N. HCl at 60° C. and 70° C., calculated in the ordinary way. The constancy in each case is good, which might well be expected in view of the large total rotational change, which can, moreover, be followed directly in the polarimeter tube at the

<sup>17</sup> The writer is indebted to Dr. W. M. Owens for making these determinations.

<sup>18</sup> *Simple Carbohydrates and Glucosides*, 4th edition, 193 (1924).

<sup>19</sup> Falk, *Chemistry of Enzyme Action*, 2nd edition, 112 (1924).

<sup>20</sup> Falk, McGuire and Blount, *J. Biol. Chem.*, 38, 229 (1919).

## HYDROLYSIS OF GLUCOSIDES

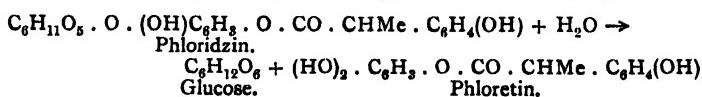
temperature required. The critical increment for the hydrolysis of arbutin is found to be 31,400 calories.

TABLE VIII.—VELOCITY CONSTANTS FOR THE HYDROLYSIS OF 10% ARBUTIN BY NORMAL HCl.

Time (Minutes).	Rotation (Degrees).	$k \times 10^6$ (Seconds <sup>-1</sup> ).	Time (Minutes).	Rotation (Degrees).	$k \times 10^6$ (Seconds <sup>-1</sup> ).
		At 60° C.			At 60° C.
0	- 26.81	—	0	- 25.60	—
76	- 19.89	4.20	50	- 21.00	4.22
98	- 18.09	4.22	71	- 19.26	4.21
150	- 14.30	4.20	100	- 16.97	4.22
237	- 8.85	4.23	500	2.14	4.23
350	- 3.55	4.20	545	3.25	4.20
423	- 0.77	4.20	600	4.62	4.24
1500	12.99	—	1500	12.95	—
	Mean	= 4.21		Mean	= 4.22
Average value of $k$ at 60° C. = $4.22 \times 10^{-5}$ Seconds					
		At 70° C.			At 70° C.
0	- 26.45	—	0	- 26.72	—
86	- 3.94	16.4	51	- 11.17	16.2
90	- 3.30	16.4	92.5	- 3.12	16.3
105	- 1.09	16.3	107	- 0.96	16.3
120	0.87	16.4	179	6.07	16.3
141	3.14	16.4	212	7.98	16.3
160	4.85	16.4	239	9.16	16.3
Inf.	13.00	—	Inf.	13.00	—
	Mean	= 16.4		Mean	= 16.3
Average value at 70° C. = $16.4 \times 10^{-5}$ Seconds <sup>-1</sup>					

### The Hydrolysis of Phloridzin.

Phloridzin is a naturally occurring glucoside which is hydrolysed by acids into glucose and phloretin (condensation product of *p*-hydroxyhydrotropic acid and phloroglucinol) according to the following equation:—



Although phloridzin is structurally the most complex glucoside examined, the measurement of its rate of hydrolysis has offered only one slight experimental difficulty, *i.e.*, its extremely low solubility in water.

The constitution of phloridzin was first established by Roser.<sup>21</sup> Rennie<sup>22</sup> identifies the sugar produced by the hydrolysis of phloridzin to be glucose by means of the melting-point of its osazone (204° C.). The value given by him for the specific rotation of the sugar, however, is + 57.9°. The infinity rotations given in Table X. indicate a still higher value (+ 58.9°) for the specific rotation of the sugar generated. The accepted value of  $[\alpha]_{D}^{20}$  for glucose is + 52.5°. The abnormally high value of the observed specific rotation cannot be explained by assuming partial

<sup>21</sup> *Annalen*, 74, 178 (1850).

<sup>22</sup> *Trans. Chem. Soc.*, 51, 634 (1887).)

condensation of glucose into diglucose, since this effect will be negligible at the concentrations of glucose considered (less than 0·5 g. per 100 c.c.). As far as can be ascertained, no measurements have been made of the rate of hydrolysis of phloridzin by means of acids or enzymes. The negative results obtained from its behaviour towards emulsin would seem to indicate that it is not a  $\beta$ -glucoside.

*The Purity and Solubility of Phloridzin.*—Commercial phloridzin appears as a yellow, light powder. To purify it, the material has been recrystallised from water. The crystals obtained after the sixth crystallisation constitute colourless, well-defined needles which contain two molecules of water of crystallisation. Table IX. below gives the values determined for the specific rotation and the melting-point of purified phloridzin, along with some of the accepted values:—

TABLE IX.

Authority.	Specific Rotation.	Melting-Point.
Thorpe ( <i>Dict. of Appld. Chem.</i> , 3, 413 (1922)).	- 50·00°	108° C.
Watts ( <i>Dict. of Chem.</i> , 4, 102 (1894)).	- 49·00°	109° C.
Moelwyn-Hughes (Measured in normal HCl at 60° C.)	- 50·02°	110·5° C.
— (Measured in absolute alcohol at 20° C.)	- 52·40°	—
— (Measured in acetone at 20° C.)	- 51·23°	—

*Experimental Procedure and Results.*—In order to measure the rate of hydrolysis of phloridzin by means of acid at 60° C., a saturated aqueous solution of the glucoside was prepared at this temperature. The solubility of phloridzin at this temperature (found in the usual way by removing a sample of the saturated solution into a tared flask, and by weighing after cooling and after the evaporation of water) is 1·578 g. per 100 g. of water. 75 c.c. of this saturated solution were transferred into a 100 c.c. stoppered flask, and 25 c.c. of 4-N. HCl were added at 60° C. A sample of the well-shaken mixture is rapidly transferred into a 4-decimetre polarimeter tube, previously heated to 60° C., by circulating water round the tube while still empty, and optical readings are taken in the usual manner. The hydrolysis of phloridzin, as already pointed out, is accompanied by the production of phloretin, which was shown by Roser<sup>21</sup> to be insoluble in water. This is precipitated quantitatively at the bottom of the polarimeter tube, and, in the concentration employed (1·183 g. of phloridzin per 100 c.c. of solution) does not affect the transmission of light. The same procedure is adopted at 70° C., except that, since the solubility in this case is 4·567 g. per 100 g. of water, the reaction mixture contains, per 100 c.c., 1·142 g. of phloridzin. The concentration of phloridzin employed at both temperatures is thus a little over 1 %. Table X. shows that the reaction follows the unimolecular law, as for glucoside hydrolyses generally. It will be noted that phloridzin is hydrolysed 2·36 times as rapidly as arbutin and 6·1 times as rapidly as salicin or maltose under the same conditions. Of the aromatic glucosides hitherto examined, phloridzin is the most labile. The critical increment of the reaction is found to be 23,100 calories.

## HYDROLYSIS OF GLUCOSIDES

TABLE X.—VELOCITY CONSTANTS FOR THE HYDROLYSIS OF PHLORIDZIN BY NORMAL HCl.

Time (Minutes).	Rotation (Degrees).	$k \times 10^5$ (Seconds $^{-1}$ ).	Time (Minutes).	Rotation (Degrees).	$k \times 10^5$ (Seconds $^{-1}$ ).
0	- 2.05	—	At 60° C.	0	At 60° C.
28	- 1.54	10.06	26	- 1.62	9.85
60	- 1.07	10.21	56	- 1.16	10.11
84	- 0.76	10.40	70	- 0.97	9.64
98	- 0.68	9.68	158	- 0.14	9.96
135	- 0.32	9.87	191.5	+ 0.11	10.19
186	0.00	9.61	303	+ 0.57	9.92
Inf.	+ 1.07	—	Inf.	+ 1.09	—
	Mean = 9.96			Mean = 9.94	
Average value of $k$ at 60° C. = $9.95 \times 10^{-5}$ Seconds $^{-1}$ .					
	At 70° C.			At 70° C.	
0	- 1.90	—	0	- 1.88	—
10	- 1.49	25.6	10	- 1.42	29.3
17	- 1.22	26.4	16	- 1.21	27.8
24	- 1.01	25.7	24	- 0.93	28.1
36	- 0.66	26.1	72	+ 0.17	29.2
43	- 0.48	26.3	94	+ 0.44	29.6
Inf.	+ 0.98	—	Inf.	+ 0.98	—
	Mean = 26.0			Mean = 28.8	
Average value of $k$ at 70° C. = $27.4 \times 10^{-5}$ Seconds $^{-1}$ .					

## Discussion of Results.

Table XI. below contains experimental values for the velocity constants and critical increments relating to the hydrolysis of certain disaccharides, trisaccharides and glucosides, the data for sucrose, raffinose, melezitose and lactose having been obtained by Dr. S. N. H. Stothart (unpublished work carried out in this laboratory), and the values for maltose hydrolysis being

TABLE XI.

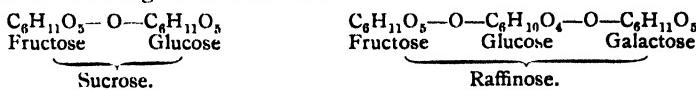
Di-saccharide, Tri-saccharide, or Glucoside.	Link Ruptured.	Unimolecular Constant by N. HCl at 60° C.	Critical Increment (Calories).
Sucrose . .	Fructoside-glucoside .	$1.87 \times 10^{-2}$	26,000
Raffinose . .	" " "	$1.41 \times 10^{-2}$	25,600 } 25,700
Melezitose . .	(Probably fructoside- glucoside). . .	$4.73 \times 10^{-3}$	25,600
Lactose . .	$\beta$ -galactoside . .	$1.98 \times 10^{-5}$	27,100
Maltose . .	$\alpha$ -glucoside . .	$1.63 \times 10^{-5}$	31,500 } 31,600
Salicin . .	$\beta$ -glucoside . .	$1.63 \times 10^{-5}$	31,900 }
Arbutin . .	$\beta$ -glucoside . .	$4.22 \times 10^{-5}$	31,400
Phloridzin . .	Type of link uncertain	$9.95 \times 10^{-5}$	23,100

those found by Dr. A. J. Kieran (also unpublished work carried out in this laboratory). The factors which govern the rate of hydrolysis are so little understood that it is questionable whether a comparison of rates of hydrolysis will lead to the elucidation of the mechanism involved. It is probable that the critical increment is a much more significant quantity than the rate of hydrolysis. The considerations based on the comparative rates of hydrolysis

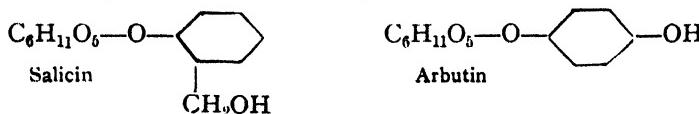
given below are of interest mainly as summarising recent contributions to the systematic study of the acidic hydrolysis of glucosides.

It may be noted that, in general, fructosides are hydrolysed more readily than glucosides or galactosides. How far it is logically permissible to compare the rates of hydrolysis of maltose and salicin is a matter of conjecture. Whereas both are glucosides, maltose is  $\alpha$ -glucosido-glucose and salicin is  $\beta$ -glucosido-salicin, from which it is evident that the groups substituted into the glucose molecule are not only different in each case but are attached to the glucose molecule in stereochemically different manners ( $\alpha$  and  $\beta$ ). Armstrong and Caldwell<sup>23</sup> have shown that the relative rates of hydrolysis of  $\alpha$ - and  $\beta$ -methyl-glucosides are as 1 : 22. It would appear, then, that the practical identity in the rates of hydrolysis of maltose and salicin is largely fortuitous. Arbutin in the presence of *N*. HCl at 60° C. is hydrolysed 2·58 times as rapidly as salicin under the same conditions. In the presence of 0·05 *N*. HCl at 77° C., the ratio is 2·56.<sup>24</sup> This result, coupled with the data obtained by the writer at 70° C., demonstrates that the relative activities of arbutin and salicin (in so far as these can be estimated by the comparison of rates of hydrolysis) are independent of the temperature and the concentration of the catalyst. Josephson<sup>24</sup> points out that the marked difference between acidic and enzymic hydrolyses is readily seen from the fact that the relative rates of hydrolysis of arbutin and salicin by means of emulsin under comparable conditions are as 1 : 11. It will be noted that phloridzin is hydrolysed 6·1 times as rapidly as salicin, and is, of the aromatic glucosides hitherto examined, the most readily hydrolysed.

Whereas a study of the rates of hydrolysis of disaccharides and glucosides does not at present lead to a rational classification of the available data, a comparison of critical increments of the reactions shows that these are much more significant quantities than velocities in that *the value of the critical increment appears to be determined largely by the nature of the link ruptured in each case, and is apparently independent of the stereochemical ( $\alpha$  or  $\beta$ ) nature of the bond and of the presence of substituted groups in the non-sugar portion of the molecule*. Thus, the biose link in sucrose is hydrolysed at a rate of  $1\cdot87 \times 10^{-2}$  seconds<sup>-1</sup> under the conditions stated. The substitution of a galactose "radicle" into the terminal hydroxyl group of the glucose residue of sucrose gives rise to the trisaccharide raffinose.<sup>25</sup>



The rate of hydrolysis of the fructoside-glucoside link in raffinose is almost 30 % lower than that of the same link in sucrose, yet the critical increment has remained sensibly the same in both cases. Consider further the cases of salicin and arbutin. The removal of the primary alcohol group —CH<sub>2</sub>OH from the *ortho* position in the benzene portion of salicin and the substitution of a phenolic group —OH in the *para* position result in an increase of 158 % in the rate of hydrolysis; the critical increment has again, however, remained substantially the same in each case.



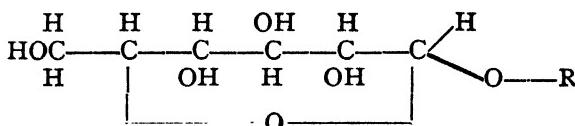
<sup>23</sup> Proc. Roy. Soc., **74**, 188 (1904).

<sup>24</sup> Josephson, Z. physiol. Chem., **147**, 1 (1925).

<sup>25</sup> Howarth, Hirst, and Ruell, Trans. Chem. Soc., **123**, 3125 (1923).

The critical increment for the hydrolysis of three fructosides (sucrose, raffinose, and melezitose) is 25,700 calories ( $\pm 1\%$ ); the critical increment for the hydrolysis of three glucosides (maltose, salicin, and arbutin) is 31,600 calories ( $\pm 1\%$ ); the critical increment for the only galactoside which has been examined (lactose) is different in value from either of these, *viz.*, 27,100 calories. As already pointed out, it would appear that the value of the critical increment of the hydrolysis in each case is governed largely by the nature of the link which is ruptured, *i.e.*, on whether it is a fructoside, glucoside, or galactoside.

Assuming the natural glucosides to be derivatives of normal glucose, we can write their general structure as follows:<sup>26</sup>



It has been shown that the critical increment is almost independent of the nature of the substituted group -R; it is, however, sensitive to re-arrangement in the sugar portion of the molecule. This would appear to suggest that in hydrolysis the primary attack by the hydrolysing agent is not upon the linkages attached to the oxygen atom forming the bridge, as it were, between the sugar and the non-sugar portions of the molecule, but is rather upon the bonds attached to the oxygen atom in the amylene-oxide ring of the sugar portion itself. If this were not the case, it would be very difficult to see how the critical increment could be virtually independent of the nature of the substituted group -R. It may be noted that this conclusion is in agreement with that arrived at by Armstrong and Glover.<sup>27</sup> The first step, therefore, in hydrolysis appears to be the momentary formation of a straight chained sugar derivative with the groups -OH and -OR attached to the terminal carbon atom; it may probably be assumed that this compound is so unstable that fission occurs as a consequence thereof.

The case of phloridzin is anomalous in the sense that the observed critical increment for this glucoside (23,100 calories) is decidedly lower than the mean value for the three other glucosides investigated (31,600 calories). Incidentally, phloridzin is distinguished biochemically also from other glucosides so far as is known in that it possesses the property of inducing progressive glucosuria in animals. It has already been pointed out that the specific rotation of the glucose generated during the hydrolysis of phloridzin is 10 % larger than the accepted value for ordinary  $\alpha$ - $\beta$  glucose. The abnormally low value for the critical increment of the hydrolysis of phloridzin, its anomalous physiological behaviour, and the exceptionally high value of the specific rotation of the parent sugar all tend to indicate that the term glucoside can hardly be applied to phloridzin in the same sense as it is applied to maltose, salicin, or arbutin.

### Summary.

- (1) The rates of hydrolysis of salicin, arbutin, and phloridzin by means of *N*. HCl have been determined at 60° C. and 70° C.
- (2) A summarising table of velocity constants and critical increments of certain disaccharides, trisaccharides, and glucosides shows that the critical

<sup>26</sup> Charlton, Howarth and Peat, *Trans. Chem. Soc.*, 350 (1926).

<sup>27</sup> *Proc. Roy. Soc., 80B*, 312 (1908).

increment of the reaction is a more significant quantity than velocity itself in that it lends itself more readily to comparative treatment.

(3) The mean value of the critical increment for three fructosides (sucrose, raffinose, and melezitose) is 25,700 calories, for three glucosides (maltose, salicin, and arbutin) is 31,600 calories, and for the only galactoside examined (lactose) is 27,100 calories. The experimental value of the critical increment seems to be determined largely by the nature (fructoside, glucoside, or galactoside) of the link ruptured and is apparently independent of the stereochemical ( $\alpha$  or  $\beta$ ) character of the bond.

(4) The critical increment for phloridzin (23,100 calories) is abnormally low. This glucoside is exceptional also in the specific rotation of the parent glucose and in its physiological action.

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## THE REACTIVITY OF GLUCOSE IN PRESENCE OF HYDROCHLORIC ACID.<sup>1</sup> PART I.

BY EMYR ALUN MOELWYN-HUGHES.

*Received 13th December, 1927, and read 29th February, 1928.*

Caldwell and Courtauld,<sup>2</sup> during their polarimetric investigation of the rate of hydrolysis of amygdalin in the presence of normal HCl at 60° C., found that the infinity rotation of the mixture was abnormal. In order to calculate a velocity constant, they employed a theoretical value for  $a_{\infty}$ , i.e., a value calculated from the knowledge of the concentration of sugar present and its specific rotation, because "prolonged action of HCl at 60° C. gives rise to secondary changes." The data of Dr. A. J. Kieran<sup>3</sup> who studied the effect of glucose on the hydrolysis of maltose, using the same catalyst at the same temperature, show anomalous values for final rotations; and the writer, who has investigated the hydrolysis of salicin under similar conditions, finds a marked discrepancy between the calculated and observed values of infinity rotations. The effect seems to be a general one for all reactions in which glucose is subjected to the prolonged influence of normal HCl at temperatures of 60° C. or above. The present work has been undertaken with a view to finding to what extent the rotation of glucose is affected by the prolonged action of fairly concentrated HCl, namely 1·0 normal at 60° C. and 70° C.

### Previous Work on the Action of Acids on Glucose.

A number of investigators have studied the effect produced by acids on glucose solutions. Most of the work has been, however, confined to the behaviour of concentrated solutions of glucose at low temperature (0° C.) in the presence of concentrated acid. Only one paper has been found

<sup>1</sup> Communicated by Professor W. C. M. Lewis.

<sup>2</sup> *Trans. Chem. Soc.*, 91, 666 (1907).

<sup>3</sup> Unpublished work carried out in this Laboratory.

dealing with the effect of dilute acid on glucose solutions at higher temperatures.

Fischer,<sup>4</sup> gave the name isomaltose to the disaccharide obtained by him by the condensing action of strong acids on glucose. His work has recently been repeated by Georg and Pictet.<sup>5</sup> Berlin<sup>6</sup> states that the substance which has been called isomaltose contains a mixture of (biose-linking) gentiobiose. Zeichmeister,<sup>7</sup> states that the reaction is reversible, i.e., prolonged action of acid on glucose solutions causes an increase in positive rotation; removal of the acid causes a decrease in positive rotation.

Harrison<sup>8</sup> has investigated the effect produced by 0·745 normal HCl on 25 per cent. and 50 per cent. solutions of glucose at a temperature of 75° C. He finds that the rotations of these solutions increase by 7 per cent. and 15 per cent. respectively after 32 hours. Harrison has also studied the effect of acids on fructose under similar conditions. By plotting graphs showing the relation of rotation to time, he is able to arrive at the velocity of the reaction in its initial stages; and by comparing two different velocities found for two different concentrations of fructose, he arrives at the conclusion that the reaction is of the second order. By analogy between the experimental curves of glucose and fructose, Harrison ascribes a second order to the condensation of glucose. That a disaccharide of high positive rotation is actually formed is shown by cryoscopic measurement, the molecular weights observed for the condensation product isolated being 326 and 332 which according to Harrison are "in sufficient agreement with the theoretical molecular weight of isomaltose 342."

#### Purity of the Glucose Employed.

The two criteria which have been employed as a means of estimating the purity of glucose are the value of its specific rotation and the reproducibility of its behaviour towards acid. Samples of glucose described as pure by chemical manufacturers were found to be impure. The glucose which has been used throughout this investigation has been prepared from commercial glucose by a method, the details of which were kindly communicated by Professor Haworth, of Birmingham. The method consists of successive crystallisation from hot absolute alcohol and hot glacial acetic acid, and gives a 40 per cent. yield of pure  $\alpha$ -glucose, which, on being dissolved in water reaches a true equilibrium value. Table I. contains the values of the specific rotations observed for solutions of glucose in water and in volume-normal HCl solutions at 20° C.

TABLE I.

Solvent.	Solute.	Grams/100 c.c.	$[\alpha]_D^{20^\circ}$ .
Water Water	Commercial glucose	10·0084	+ 51°24°
	Purified glucose	3·9564	52°25°
Normal HCl	Purified glucose	8·0037	52°56°
		11·7512	52°60°
		10·0335	52°90°
		20·0970	52°90°
		30·0393	53°27°

<sup>4</sup> Berichte, 23, 3687 (1890).<sup>5</sup> J. Amer. Chem. Soc., 98, 1107 (1926).<sup>6</sup> J. Amer. Chem. Soc., 36, 586 (1914).<sup>7</sup> Helv. Chim. Acta., 9, 612 (1926).<sup>7</sup> Z. physik. Chem., 103, 316 (1922).

It will be noticed that the value of  $[a]_D^{20}$  is slightly greater when the sugar is dissolved in *N*. HCl than when the measurement is made in pure water. This effect is an immediate one reached at room temperatures, and must not be confused with the prolonged action of HCl at higher temperatures.

### Experimental Results.

100 c.c. stoppered flasks containing 10, 20, 30, 40 and 50 grams of glucose in volume-normal HCl were kept in a thermostat regulated at 60° C. Samples of the five solutions were removed at intervals. The reaction was stopped by chilling the samples in ice-cold water, and the rotations of the solutions were taken in a 4-decimetre polarimeter tube at room temperatures. Concentrated solutions of glucose removed during advanced stages of the reaction were decolorised by shaking with a small quantity of Merck's powdered medicinal charcoal. The rotations of the five solutions were taken daily for eight days. Table II. contains the data obtained from duplicate experiments.

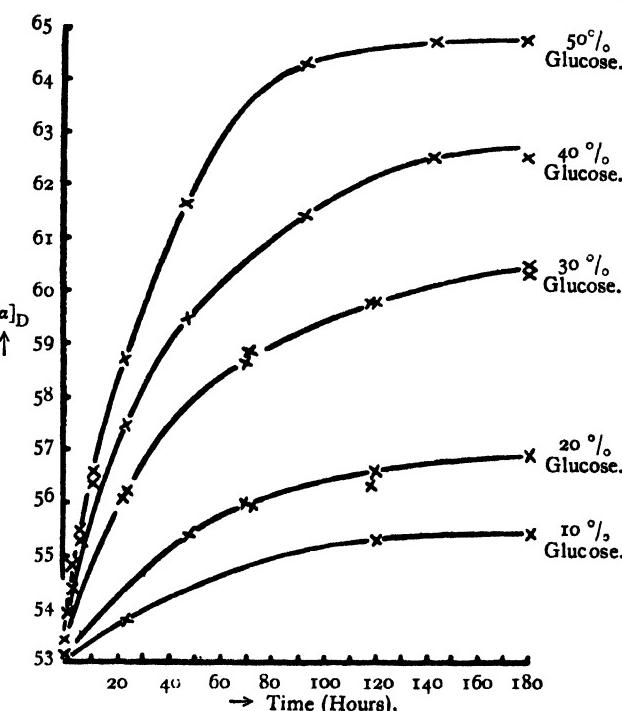


FIG. I.—The Effect of *N*. HCl at 60° C. on the Specific Rotation of Glucose.

The curves show the effect produced by *N*. HCl on the *specific* rotation of glucose solutions at 60° C. In each case, the rotation reaches a limiting value within 200 hours; in the case of the more concentrated solutions, the reaction has been followed for 330 hours, but the rotations taken at this time differ by less than 0.5° from the rotation taken at time 200 hours. There is no indication of a maximum in any of the curves.

In the second column of Table III. are given the values of the total increase in rotation exhibited by the solutions: each value is a mean of two, which differ by not more than 0.2° from the mean. The third column contains the percentage increase in rotation in each case. That the values are a measure of the extent of conversion in each case may be shown as follows. Let:—

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$\alpha_{\infty}$  = observed infinity rotation.

$\alpha_0$  = observed initial rotation.

$\alpha_1$  = specific rotation of reactant (glucose).

$\alpha_2$  = specific rotation of resultants (di-glucose).\*

$c$  = mass of glucose per 100 c.c. of solution at the beginning of the reaction.

$x$  = mass of di-glucose per 100 c.c. of solution at the end of the reaction.

TABLE II.

Time (Hours)	Rotation of Solutions.				
	10 Per Cent.	20 Per Cent.	30 Per Cent.	40 Per Cent.	50 Per Cent.
0	21°43	42°54	64°45	84°86	107°05
1	—	—	—	—	107°66
3	—	—	—	86°74	109°56
6	—	—	—	87°84	110°87
11	—	—	—	89°50	113°06
22	—	43°70	67°79	—	—
23	—	—	—	91°20	117°30
24	21°78	43°85	67°99	—	—
47	—	—	—	94°30	123°21
48	—	44°35	—	—	—
70	—	44°81	70°91	—	—
72	22°11	44°75	71°13	—	—
94	—	—	—	98°23	128°43
118	—	45°07	72°27	—	—
120	22°40	45°29	72°30	—	—
144	—	—	—	99°28	129°27
200	—	45°60	—	—	—
Inf.	22°44	45°75	73°15	99°35	129°40

TABLE III.

Grams Glucose per 100 c.c. Solution.	$(\alpha_{\infty} - \alpha_0)$ (Degrees).	Percentage Increase in Rotation $100 \left( \frac{\alpha_{\infty} - \alpha_0}{\alpha_0} \right)$ .	Relative Fractional Increases.	Time of Half-Completion (Hours).
10	1°01	4°71	1°2	40
20	3°42	8°04	2°0	38
30	8°69	13°48	3°4	35
40	14°49	17°08	4°3	29
50	22°36	20°84	5°2	26

Assuming the mixture law to be valid for the rotations of the resultants :—

$$\alpha_{\infty} = \frac{1}{25} \{ (c - 1.05x) \alpha_1 + x \alpha_2 \}$$

$$\alpha_0 = \frac{1}{25} \cdot c \alpha_1$$

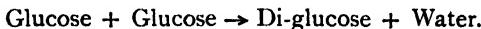
The term  $\frac{1}{25}$ , which is the ratio of the length of the polarimeter tube (4 dms.) to the volume of solution (100 c.c.) containing  $c$  grams of solute, is a constant which appears in the equation used to calculate specific

\* This non-committal term is used to designate the products of the condensation of glucose, without specifying the nature of the sugars produced.

rotations. If  $x$  grams of di-glucose are produced,  $1\cdot05 \left( i.e., \frac{2 \times 180}{342} \right)$  grams of glucose have undergone condensation.

$$\text{Further, } \frac{a_{\infty} - a_0}{a_0} = \left( \frac{a_2 - 1\cdot05a_1}{a_1} \right) \cdot \frac{x}{c}.$$

The fractional increase of rotation is proportional to the mass of di-glucose present at equilibrium and is, therefore, an indication of the extent of chemical change. It will be seen from column 4 of the above table that the fractional increase in rotation is proportional to the initial concentration of glucose present. This would indicate that the reaction is of the second order, as would be expected from the stoichiometric form of the equation :—



On the other hand, the times of half-completion of the reaction, which have been determined graphically from rotation-time curves, are in the ratio of  $1\cdot00$ ;  $0\cdot95$ ;  $0\cdot88$ ;  $0\cdot73$ ;  $0\cdot65$  for  $10$ ,  $20$ ,  $30$ ,  $40$ , and  $50$  per cent. solutions respectively. If the reaction were of the second order, the times of half completion would be in the ratio of  $1\cdot00$ ;  $0\cdot50$ ;  $0\cdot33$ ;  $0\cdot25$ ;  $0\cdot20$ . Although the observed times of half-completion are apparently not independent of the initial concentration of glucose, as would be expected if the reaction were unimolecular, the values certainly do not conform to a possible bimolecular reaction.

Table IV. contains the data employed in the van't Hoff differential method for determining the order of the reaction. The values in the second column are the rate of change in rotation at  $60^{\circ}\text{C}$ ., which govern the initial stages of the reaction : they are evaluated graphically, by considering the first  $10$  hours only. The third column gives values for the rate of change of rotation in degrees per second divided by the total rotational change in each case : these values should approximate to constancy if the reaction is of the first order, whereas actually they are seen to increase with increase in concentration of glucose—a result which is in harmony with the observation that the times of half-completion decrease with increase in concentration of glucose. The reason for this is pointed out later. The fourth column contains the values determined for the order of the reaction. It would appear from this that the reaction is of the first order.

TABLE IV.

Grams Glucose per 100 c.c. of Solution.	$\frac{da}{dt} \times 10^6$ degrees/seconds	$\frac{1}{a_{\infty} - a_0} \cdot \frac{da}{dt} \times 10^6 (\text{sec.}^{-1})$	Order of Reaction.
10	0·44	4·40	
20	1·67	4·88	
30	4·76	5·47	
40	11·22	[7·74]	
50	16·11	7·20	
			$\left. \begin{array}{l} 1\cdot085 \\ 1\cdot102 \\ 1\cdot047 \end{array} \right\}$

It now becomes necessary to apply the unimolecular velocity constant equation to the data given in Table II. The results are shown below in Table V. The unimolecular velocity constant equation is found to hold

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for the greater part of the reaction, its applicability being least during the initial stages. On the whole, the constants in any one column are found to agree with the mean to as good an extent as can be expected, when the magnitude of the rotational change and the time are considered. It would appear, however, that the value of the uni-molecular constant is dependent on the initial concentration of glucose. That this is so is not surprising when it is recollect that the activity of the hydrogen ion in volume-normal solutions of acid is enhanced by the addition of sugar.

TABLE V.

Time (Hours).	Unimolecular Velocity Constants $\times 10^6$ Seca. $-1$ at 60° C.			
	20 Per Cent.	30 Per Cent.	40 Per Cent.	50 Per Cent.
20	—	—	—	7.53
30	—	—	6.31	7.85
40	—	5.57	6.49	7.43
50	4.69	5.47	5.94	7.85
60	5.00	5.63	6.45	7.63
70	4.92	5.46	6.25	—
80	4.49	5.47	6.88	—
90	4.61	5.45	—	—
100	4.85	—	—	—
Mean =	4.76	5.51	6.39	7.66

Jones and Lewis<sup>9</sup> have determined electrometrically the activity of hydrogen ion in the presence of sucrose. Dr. Kieran in this Laboratory has found that the activity of hydrogen ion in maltose solutions, and in solutions containing maltose and glucose, is the same as the values published by the above authors under the same conditions. Kieran concludes that the activity of hydrogen ion (in volume-normal solutions) is determined by the total mass of sugar present, irrespective of its nature. It may be inferred from this that the relative activities of hydrogen ion in volume-normal HCl solutions containing 10, 20, 30, 40, and 50 grams of glucose per 100 c.c. will be identical with the relative activities of hydrogen ion in volume-normal HCl solutions containing 10 grams maltose; 10 grams maltose + 10 grams glucose; 10 grams maltose + 20 grams glucose, etc. In Table VI, below are given the values of the activities of hydrogen ion determined by Kieran for volume-normal solutions of HCl containing 10,

TABLE VI.

Grams Glucose per 100 c.c. Solution.	Relative Activities of Hydrogen Ion, $a_{H^+}$ .	Observed Unimolecular Constants.	$\frac{k_{obs}}{a_{H^+}} \times 10^6$ (60° C.).
10	0.97	4.20 *	4.33
20	1.11 *	4.76	4.29
30	1.27	5.51	4.34
40	1.46 *	6.39	4.38
50	1.67	7.66	4.58

\* Values marked with an asterisk have been inter- and extrapolated graphically.

<sup>9</sup> Trans. Chem. Soc., 117, 1120 (1920).

30, 50 grams of total sugar. The values in the last column demonstrate that the unimolecular constant, reckoned per unit activity of hydrogen ion, is but slightly affected by the concentration of glucose undergoing change. A similar behaviour is exhibited by the system at 70° C. This result, coupled with the mean value of 1·08 for the order of the reaction derived by van't Hoff's method, is taken as evidence that the condensation of glucose in the presence of dilute acids proceeds according to the unimolecular law, a conclusion which differs from that arrived at by Harrison.<sup>8</sup>

### A Possible Explanation of the Order of the Reaction.

The reaction considered is the partial conversion of glucose into di-glucose, which may be written in the form:—



That glucose is not decomposed into products of lower molecular weight by the action of *N*. HCl is evident from the fact that the infinity rotation is constant. The observed order of the reaction may be explained by assuming the change to be a pseudo-unimolecular reaction similar to the hydrolysis of disaccharides, in which the concentration of one of the reactants is so great compared with the concentration of the other reactant, that the former may be considered constant. Designating the variety of glucose which is present in very small concentrations as glucose,\* the reaction considered may be expressed in the following form:—



The suggestion may therefore be made that as a result of the prolonged action of *N*. HCl on glucose solutions, condensation takes place not between  $\alpha$ - and  $\beta$ -glucose (which are present in the ratio of 37·5 to 62·5) but between  $\alpha$ - or  $\beta$ -glucose and a modification of glucose which is present in very small amounts.

This explanation is in harmony with the present view regarding the composition of aqueous solutions of glucose. Irvine's<sup>10</sup> new methyl-glucoside is characterised by its capacity to undergo auto-condensation: the activity of the parent glucose from which it is derived far exceeds that of  $\alpha$ -  $\beta$ -glucose. Armstrong and Hilditch<sup>11</sup> find that acid solutions of glucose will reduce potassium permanganate solutions, whereas pure aqueous  $\alpha$ - or  $\beta$ -glucose will not. The active agent is described by them as an ethylene-oxide modification of glucose. Neuberg and Kobel<sup>12</sup> find it necessary, in interpreting the results of experiments on the behaviour of alkaline glucose towards amino-acids, to assume that not only  $\alpha$ - and  $\beta$ -glucose react with  $-\text{NH}_2$  but that a glucose with a possibly free aldehyde group similarly reacts. This view was first advanced by Euler and Josephson<sup>13</sup> and is shared by Groot.<sup>14</sup> Finally Lowry<sup>15</sup> assumes that aqueous glucose contains, in addition to  $\alpha$ - and  $\beta$ -glucose, a third modification which is in dynamic equilibrium with the other two. It is almost universally accepted that there is present in aqueous solutions of glucose, a predominating amount of  $\alpha$ -  $\beta$ -glucose, and a small quantity of a third modification. For the purposes of supporting the explanation given above, it is sufficient to assume that the quantity of the third modification is small, and that it is characterised by its capacity to condense with  $\alpha$ -  $\beta$ -glucose, without making any assumption as to its possible structure beyond implying,

<sup>10</sup> *Trans. Chem. Soc.*, 107, 524 (1915).

<sup>11</sup> *Ibid.*, 116, 1410 (1919).

<sup>12</sup> *Biochem. Z.*, 174, 464 (1926).

<sup>13</sup> *Ibid.*, 153, 3 (1926).

<sup>14</sup> *Ibid.*, 146, 90 (1924).

<sup>15</sup> *Trans. Chem. Soc.*, 127, 1371 (1927).

however, that there is a third glucose structurally different from  $\alpha$ - or  $\beta$ -glucose.

Whilst the foregoing interpretation is consistent in itself, we must not overlook the fact that the pseudo-unimolecular nature of the condensation may be explained on the usual lines of physical (thermal) activation (involving statistical distribution of internal energy amongst the molecules of the system), a small number of the molecules of the structurally normal ( $\alpha$  and  $\beta$ ) forms being active as regards energy content, such "specialised" molecules being capable therefore of reacting with  $\alpha$ - or  $\beta$ -glucose molecules of average energy content to produce the condensation. If this be the real mechanism involved the determination of the critical increment of the pseudo-unimolecular process becomes of some importance.

The following table contains the unimolecular velocity constants at  $60^\circ$  C. and  $70^\circ$  C. corresponding to initial concentrations of glucose of 40 and 50 grams per 100 c.c. respectively. With these initial concentrations, the velocity constants are believed to be somewhat more reliable than with more dilute solutions. The final column of the table contains the critical increment.

Per Cent. Glucose.	$k \times 10^6$ (secs. $^{-1}$ ) at $60^\circ$ C.	$k \times 10^6$ (secs. $^{-1}$ ) at $70^\circ$ C.	Critical Increment (Calories).
40	6.39	2.84	34,080
50	7.66	3.29	33,310

From the velocity constants at the two temperatures, it is found that the critical increment is in round figures 33,500 cals. That is, one mole of structurally normal glucose possessing the average internal energy corresponding to the temperature requires this very considerable amount of energy to render it active in the physical sense. Experience of numerous other reactions leads us to anticipate values lying usually between 15,000 and 30,000 cals. for the critical increment. The inversion of sucrose for example requires 26,000 cals.; hydrolysis of maltose 31,500; hydrolysis of amygdalin, 35,200. The relatively high value for the critical increment in the glucose condensation process is therefore quite a reasonable one to anticipate without making any appeal whatsoever to the concept of a  $\gamma$  or structurally reactive form. In fact, if the structurally reactive form exists (even for a limited time) and participates in the condensation process, we would expect a very low critical increment as otherwise it is difficult to see how any significance can be attached to the term reactive as applied to structure. This statement is not intended to suggest that structural reactivity and physical (thermal) activation are identical or similar. It would be quite logical to speak of a structurally active form having the average or normal energy content characteristic of that structure. It would seem reasonable, however, to conclude that a structurally reactive form should require a decidedly smaller increment of energy to cause it to enter into combination or to decompose. The fact that the observed critical increment is high is so far as it goes evidence decidedly in favour of physical activation as opposed to the interposition of a structurally reactive form possessing a definite chemical existence. Incidentally, if the  $\gamma$  form is present and participates, we should find a critical increment actually lower than the relatively low one expected on *a priori* grounds, for we may infer from the statement of Howarth<sup>16</sup> that the  $\gamma$  form is diminished

<sup>16</sup> *Trans. Chem. Soc.*, 2468 (1924).

in amount by an increase in temperature and consequently the velocity at the higher of two temperatures is not increased to the extent it ought to be and would be if the concentration of the  $\gamma$  form had remained the same at both temperatures.

We have now considered with as great impartiality as possible the two possible modes of activation, one of which is operative in the process under review and we purposely refrain from expressing a definite opinion at this stage. Certain suggestions which the writer owes to Professor I. M. Heilbron are being investigated in the hope that sufficient evidence of a decisive character may ultimately be forthcoming.

One point remains to be mentioned, namely the unexpectedly great stability of the di-glucose produced. If this were a disaccharide of the ordinary type, the conditions employed should have favoured its extensive hydrolysis, not its formation. It is possible that we are dealing with an anhydro ring compound. This possibility is under investigation.

### Summary.

(1) The change in rotation of 10, 20, 30, 40 and 50 per cent. solutions of glucose in *N*. HCl has been investigated at 60° and 70° C. The effect referred to exists quite apart from the familiar muta-rotation which completes itself with immeasurable rapidity under these conditions. The change in rotation is ascribed to the formation of a condensation product "di-glucose." Condensation reaction has already been demonstrated by earlier workers.

(2) The reaction is shown to be of the first order—a result which differs from that hitherto accepted.

(3) The critical increment of the process is found to be 33,500 cals.

(4) The order of the reaction is explained by assuming the condensation of glucose under the conditions of the experiment to be a pseudo-unimolecular change, in which the concentration of one of the reactants (normal glucose) far exceeds that of the other (active glucose). The nature of this "reactive form" is discussed.

The writer is indebted to Professor W. N. Haworth, of Birmingham, for valuable suggestions regarding the preparation of glucose, to the Department of Scientific and Industrial Research for a partial maintenance grant, and to Messrs. Brunner, Mond & Co. for a grant made to the Department of Physical Chemistry of the University of Liverpool.

*Muspratt Laboratory of Physical and Electrochemistry,  
University of Liverpool.*

### Discussion.

**Prof. Lowry** agreed with the author that the changes which he had studied had nothing at all to do with mutarotation. The proportions of the various sugars in an aqueous solution of glucose were still entirely unknown, although there was clear evidence of the presence of a third sugar, but in the case of galactose recent experiments had shown that the proportion of the intermediate sugar could be estimated at 12 per cent. The condensation studied by the author required that the reactive molecules of the sugar should be comparable with the minute trace of enol, which

served to explain the equilibrium between glucose, mannose and fructose, in presence of strong caustic soda, as studied by Lobry de Bruyne.

Prof. Lowry also referred to the advantage of using a mercury lamp instead of a sodium flame as a source of monochromatic light in polarimetry, and added that a sugar which gave  $[\alpha]_D = +59^\circ$  ought not to be described as glucose, although it might be a mixture containing this sugar.

**Mr. Moelwyn-Hughes**, in reply, agreed with Prof. Lowry that the composition of aqueous solutions of glucose was still unknown, but pointed out that the explanation given in the paper required only that aqueous solutions of glucose (whatever its composition) should contain, in the presence of acid, one variety of glucose in very small amounts.

## VAPOUR-PRESSURE AND HEAT OF DILUTION OF AQUEOUS SOLUTIONS. PART V.—ACTIVITY.

BY EDGAR PHILIP PERMAN.

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Numerous measurements of the vapour-pressure of aqueous solutions made recently by myself and co-workers lend themselves to the calculation of the activities of the constituents of the solutions.

*Cane Sugar.*—One of the most interesting cases is that of cane sugar. Using the results of Downes and Perman<sup>1</sup> a dilute solution of cane sugar proves to be not appreciably different from a perfect solution. Taking the vapour pressures at 80° C. and using the notation of G. N. Lewis, the results in Table I. are obtained:—

TABLE I.—CANE SUGAR SOLUTION.

Temp.	$\frac{n}{N}$	$N_1$	$a_1$	$\frac{a_1}{N_1}$	$\frac{a_2}{N_2}$
80° C.	.004145	.9959	.9972	1.001	1.000
	.01328	.9869	.9904	1.004	1.000
	.01780	.9825	.9871	1.005	1.000
	.02667	.9740	.9764	1.002	1.000
	.03985	.9616	.9626	1.001	1.000
	.05197	.9506	.9446	.9937	1.154
	.06709	.9371	.9249	.9869	1.321
	.08809	.9190	.8857	.9638	1.721
	.09848	.9103	.8689	.9545	1.948
	.1249	.8890	.8279	.9313	2.436

The activity of the water  $a_1$  is given by the ratio of the vapour-pressure of the solution to the vapour-pressure of water at the same temperature, i.e., the activity of water at the same temperature is taken as the standard

$N_1 = \frac{N}{N+n}$  (usual notation). For pure water therefore  $\frac{a_1}{N_1} = 1$ , and the

departure from unity of  $\frac{a_1}{N_1}$  measures the variation from a perfect solution.

In this case it is seen that up to a strength of  $\frac{n}{N} = .04$  the solution may be

<sup>1</sup> *Trans. Faraday Soc.*, 23, 101, 1927.

taken to be perfect, and up to  $\frac{n}{N} = .07$  the deviation is very small. The fact that the solution is perfect up to a considerable concentration makes it an easy matter to calculate  $a_2$  the activity of the solute.

Taking  $N_2 = \frac{n}{N+n}$ , then  $-\int_0^{N_2} \frac{N_1}{N_2} dz \log \frac{a_1}{N_1} = \log \frac{a_2}{N_2}$ <sup>2</sup>

A graphic integration gives the values for  $\frac{a_2}{N_2}$  shown in the preceding table;  $a_2$  is here taken as 1 in an infinitely dilute solution. The activity of the solute is therefore proportional to  $\frac{n}{N+n}$  ( $= N_2$ ) up to about 500 g. per litre. At greater concentrations the deviation increases and is due probably to the volume of the solute molecules.

Similar results have been obtained at 70° C. and 50° C., but the lower the temperature, the lower the concentration at which the solution becomes imperfect.

The results are given in concise form in Tables II. and III. It is assumed in these calculations that water vapour under the experimental conditions acts as a perfect gas; this assumption appears to be justified by the fact that the vapour-pressure of these solutions are identical whether determined by the statical or the air-bubbling method.

TABLE II.—CANE SUGAR SOLUTION.

Temp.	$\frac{n}{N}$	$N_1$	$\frac{a_1}{N_1}$	$N$	$\frac{a_2}{N_2}$
70° C.*	.004604	.9954	1.0016	—	—
	.006973	.99305	1.0031	—	—
	.01032	.9898	1.0004	.0102	1.000
	.01487	.9853	.9995	—	—
	.02146	.97895	.9994	—	—
	.03033	.9706	.9994	.0294	1.037
	.05404	.9488	.9920	.0512	1.256
	.07449	.9307	.9835	.0693	1.442
	.1027	.9089	.9558	.0931	2.007
50° C.†	.0055993	.9940	.9999	.0060	1.000
	.01382	.9864	1.0071	.0136	1.000
	.01773	.9826	.9974	.0174	1.134
	.02435	.9762	.9933	.0238	1.269
	.03472	.9665	.9950	.0335	1.437
	.04615	.9559	.9914	.0441	1.624
	.05939	.9439	.9852	.0561	1.847
	.07259	.9323	.9699	.0677	2.053
	.09906	.9098	.9626	.0902	2.427
	.12216	.8911	.9347	.1089	2.801

\* Here the solution is taken as perfect up to a strength of  $\frac{n}{N} = .01$ , but there is very little departure from this condition up to  $\frac{n}{N} = .03$ .

† In this case the solution is taken up as perfect up to  $\frac{n}{N} = .014$ .

<sup>2</sup> Lewis and Randal, *Thermo Dynamics*, p. 271, 1923.

The values of  $\frac{a_1}{N_1}$  have been calculated also for the results of Berkeley, Hartley, and Burton.\*

TABLE III.—CAKE SUGAR SOLUTION.

Temp.	Gm. per 100 gm. Water.	$N_1$ .	$\frac{\rho_0}{\rho_1}$	$\frac{a_1}{N_1}$
30° C.	33·94	·9824	1·01960	·9983
	56·71	·9710	1·03500	·9950
	81·21	·9590	1·0539	·9894
	111·89	·9444	1·0806	·9800
	141·26	·9308	1·1089	·9689
	182·94	·9122	1·1530	·9508
	217·63	·8972	1·1924	·9347
0·4° C.	56·63	·9710	1·0359	·9941
	81·27	·9590	1·0553	·9881
	112·12	·9443	1·0827	·9781
	141·18	·9308	1·1127	·9655
	182·80	·9122	1·1580	·9467
	218·15	·8970	1·1990	·9298
	243·19	·8865	1·2301	·9170

From these results it is clear that the higher the temperature the higher the concentration at which the solution remains perfect. It is of interest also to compare the values of  $\frac{a_2}{N_2}$  at the same concentration. For  $\frac{N_1}{N_2} = 10$ , at 50°  $\frac{a_2}{N_2} = 2·43$ , at 60° 2·05 and at 80° 1·94, thus showing an increased departure from the perfect state at the lower temperatures.

The ratio of the vapour densities  $\frac{\rho_0}{\rho_1}$  tabulated by Berkeley is the reciprocal of the activity  $(\frac{P_1}{P_0})$ . The results show that the departure from normality is greater than at higher temperatures; in no case is the solution quite perfect.

*Urea.*—As urea is a non-electrolyte and forms no hydrates, it would be expected to form a solution at least as perfect as cane sugar. The activities calculated from the results of Perman and Lovett<sup>4</sup> show the solutions as apparently *more than perfect*. I attribute this to a slight hydrolysis of the urea, which undoubtedly takes place, with the formation of traces of ammonia.

Typical results are given in Table IV.

A special experiment was made to discover what amounts of ammonia were formed, the ammonia being estimated by the Nessler test. It was found that 200 c.c. of urea solution containing 5 g. urea, after boiling out the air and heating for 2 hours at 70° C., contained 2 mg. ammonia; stronger solutions would contain more, but in the vapour-pressure experiments the amounts would vary according to the time of heating, and especially the time of heating after boiling out. The amount of ammonia

\* *Trans. Roy. Soc.*, 218, A. 295.

<sup>4</sup> *Trans. Faraday Soc.*, 22, 1, 1926.

TABLE IV.—UREA SOLUTION.

Temp.	$\frac{n}{N}$	$N_1$ .	$a_1$ .	$\frac{a_1}{N_1}$ .
80° C.	.0450	.9569	.9846	1.029
	.1188	.8938	.9217	1.031
	.1941	.8375	.8618	1.029
	.2488	.8008	.8190	1.023
	.3929	.7179	.7427	1.035
	.6522	.6053	.6249	1.032
	.8553	.5390	.5558	1.031
	1.0422	.4897	.4922	1.005
	1.2458	.4453	.4518	1.015
60° C.	.0231	.9774	.9847	1.007
	.0690	.9355	.9556	1.022
	.1339	.8819	.8988	1.019
	.2537	.7976	.8176	1.025
	.4160	.7062	.7377	1.045
	.5188	.6584	.6868	1.043
	.8127	.5517	.5647	1.024

found is sufficient to cause the deviations in  $\frac{a_1}{N_1}$  from unity at the lower concentrations. At the higher concentrations  $\frac{a_1}{N_1}$  tends to fall in the same way as for cane sugar solutions. Allowing for the error caused by the presence of ammonia, urea appears to form a perfect solution up to  $\frac{n}{N} = .8$  at 80°, and up to  $\frac{n}{N} = .5$  at 60°.

If  $\frac{a_1}{N_1}$  is taken = 1, then of course  $\frac{a_2}{N_2} = 1$  over the same range.

Calculations of  $\frac{a_1}{N_1}$  have been made from the experiments of Perman and Price on urea,<sup>5</sup> and exactly similar results were obtained. In this case the air-bubbling method was used.

*Potassium Chloride.*—The activity of the water falls off regularly with increase of concentration in the usual way. The calculation of  $a_2$  is difficult as the  $\frac{N_1}{N_2}$  against  $\frac{a_1}{N_1}$  curve runs off to infinity, and the integration cannot be effected. In order to overcome this difficulty in the simplest possible way,  $\frac{a_2}{N_2}$  was taken = 1 at a dilution of  $\frac{N_1}{N_2} = 10,000$  instead of at infinite dilution. The integration can then be carried out with ease. It is not likely that  $\frac{a_1}{N_1}$  changes much between this concentration (about centi-normal) and infinite dilution, so that the error introduced will be small. The values of  $\frac{a_1}{N_1}$  for the most dilute solutions were obtained by graphical interpolation. The results are given in Table V. It is seen that  $\frac{a_2}{N_2}$

<sup>5</sup> *Trans. Faraday Soc.*, 8, 1, 1912.

reaches a high value at the greater concentrations and is greater at the lower temperature.

TABLE V.—POTASSIUM CHLORIDE SOLUTION.\*

Temp.	$\frac{N}{N_1}$	$N_1$	$\frac{a_1}{N_1}$	$\frac{N_1}{N_2}$	$\frac{a_2}{N_2}$
80° C.	.0001	.9999	.99995	10,000	1.00
	.00025	.99975	.99987	4,000	1.62
	.0005	.9995	.99975	2,000	2.45
	.0010	.9990	.9995	1,000	3.59
	.0020	.9980	.9990	500	5.25
	.00674	.9933	.9967	148.3	9.10
	.01328	.9869	.9930	75.3	13.73
	.0252	.9754	.9854	39.65	21.39
	.0313	.9697	.9811	32.00	25.03
	.0431	.9587	.9700	23.21	34.26
	.0552	.9479	.9569	18.19	45.38
	.0711	.9336	.9382	14.07	62.39
	.0904	.9171	.9118	11.06	89.29
	.1036	.9061	.8977	9.65	104.9
	.1245	.8873	.8797	7.87	125.3
60° C.	.0001	.9999	.99995	10,000	1.00
	.00025	.99975	.999875	4,000	1.70
	.0005	.9995	.99975	2,000	2.49
	.0010	.9990	.9995	1,000	3.64
	.0020	.9950	.9990	500	5.27
	.0050	.9950	.9975	200	8.93
	.0095	.9906	.9946	105.4	13.93
	.0131	.9871	.9934	76.5	15.56
	.0212	.9792	.9870	47.4	23.17
	.0296	.9713	.9799	38.8	31.63
	.0370	.9643	.9710	27.0	42.66
	.0458	.9562	.9596	21.8	56.89
	.0666	.9376	.9387	15.03	85.31
	.0790	.9268	.9280	12.66	100.00
	.0984	.9104	.9101	10.16	125.0
	.1011	.9008	.8945	9.08	147.6

It was thought worth while to calculate the activity coefficient  $\gamma$  from these results in order to compare them if possible with  $\gamma$  obtained from measurements of *E.M.F.* in dilute solutions. Since  $\frac{a_2}{N_2}$  has been taken = 1 at a concentration of  $N_2 = .0001$ ,  $\gamma$  will be 1.80 at that concentration, and for all dilute solutions it will be considerably in error. An attempt has been made to correct  $\gamma$  for results at 80° C. It shows a minimum at a little over twice normal strength, and the value changes slowly in this region. A curve was drawn of  $\gamma$  against  $\sqrt{m}$  (molality), and then a similar curve making  $\gamma = 1$  at molality .00555, instead of 1.8, and running to the same minimum as before was drawn. From this curve corrected values were read. The numbers are given in Table VI.:

\* The interpolated values of  $\frac{a_1}{N_1}$  are above the space.

TABLE VI.—POTASSIUM CHLORIDE SOLUTION.

Temp.	<i>m.</i>	<i>a<sub>1</sub></i> .	<i>a ±.</i>	$\gamma \left( = \frac{a \pm}{m} \right)$ .	$\gamma$ . (Corrected).
80° C.	.00555	.0001	.0100	1.800	1.00
	.01388	.000405	.0201	1.450	.92
	.02776	.001225	.0355	1.279	.84
	.05551	.00359	.0599	1.079	.79
	.11102	.01050	.1025	.943	.72
	.3741	.06100	.2470	.660	.59
	.7372	.1799	.4241	.575	.54
	1.399	.5262	.7254	.519	.51
	1.737	.7584	.871	.501	.50
	2.392	1.415	1.190	.497	minimum
	3.064	2.304	1.538	.502	—
	3.947	4.143	2.035	.516	—
	5.018	7.402	2.721	.542	—
	5.751	9.850	3.138	.546	—
	6.911	14.12	3.758	.544	—

The corrected value of  $\gamma$  for  $m = 1$  is 0.52. The results for 60° C. have been treated in the same way, and  $\gamma$  show a minimum at  $m = 1.64$ , the value being 0.58. For  $m = 1$  (approximately normal)  $\gamma = 0.60$ . This compares with 0.634 found by Lewis at 25° C.<sup>6</sup> Our results at 40° C are hardly sufficiently accurate, the pressures being so small, to make it worth while to derive  $\gamma$  in the same way. It is interesting to note that Harned<sup>7</sup> found a minimum value of  $\gamma$  at a concentration of about 2N at lower temperatures.

The activities have been calculated in the same way for calcium chloride solutions, except that at 80° the value of  $\frac{a_1}{N_1}$  approaches so rapidly that of N<sub>1</sub> that it was taken as equal to it for the very dilute solutions. For the results at 50° graphical interpolation was employed.

The activity of the calcium chloride reaches an enormous value at high concentrations, and this is what would be expected from the great affinity between calcium chloride and water. The activity increases with concentration very much more rapidly than that of potassium chloride, and consequently some error is involved in taking  $\frac{a_2}{N_2} = 1$  at a concentration  $\frac{N_1}{N_2} = 10,000$ . There will be obviously some change in the solution even below that concentration. The numbers obtained however are correct as compared with this artificial standard.

The activity is very much greater at 50° than at 80°, as would be expected from the smaller solubility.

*Activity and Heat of Dilution.*—The relation between activity (of the water) and heat of dilution is given by the equation,

$$H = RT^2 \frac{\partial}{\partial T} (-\log_e a_1).$$

The heats of dilution of these solutions (except cane sugar) have already been calculated from Kirchhoff's equation, so that it does not appear worth while to calculate them from the same equation put in another form.

<sup>6</sup>Loc. cit., p. 360.

<sup>7</sup>J. Amer. Chem. Soc., 38, 1989, 1916.

TABLE VII.—CALCIUM CHLORIDE SOLUTION.

Temp.	$\frac{n}{N}$	N <sub>1</sub>	$\frac{a_1}{N_1}$	$\frac{N_1}{N_2}$	$\frac{a_2}{N_2}$
80° C.	.0001	9999	9999	10,000	1.00
	.00025	99975	99975	4000	3.09
	.0005	9995	9995	2000	5.25
	.0010	9990	9990	1000	10.84
	.0020	9980	9980	500	23.17
	.0048	9952	9946	208	77.45
	.0100	9901	9839	100	410.2
	.0233	9772	9634	42.9	1845
	.0364	9649	9215	27.5	8831
	.0516	9509	8510	19.4	5.77 × 10 <sup>4</sup>
	.0741	9310	7280	13.5	7.52 × 10 <sup>5</sup>
	.1117	8995	5336	8.95	2.45 × 10 <sup>7</sup>
	.1599	8621	3681	6.25	4.12 × 10 <sup>8</sup>
	.2176	8213	2587	4.60	2.79 × 10 <sup>9</sup>
	.2491	8006	2221	4.01	5.37 × 10 <sup>9</sup>
50° C.	.0001	9999	99973	10,000	1.00
	.00025	99975	99933	4000	15.5
	.0005	9995	99867	2000	114.8
	.0010	9990	9972	1000	1047
	.0020	9980	9945	500	8035
	.0052	9948	9868	191.3	1.175 × 10 <sup>5</sup>
	.0133	9869	9868	75.3	9.98 × 10 <sup>5</sup>
	.0213	9792	9594	47.1	2.09 × 10 <sup>6</sup>
	.0263	9744	9519	38.1	2.92 × 10 <sup>6</sup>
	.0381	9633	9033	26.2	1.57 × 10 <sup>7</sup>
	.0641	9398	7635	15.6	5.28 × 10 <sup>8</sup>
	.0832	9232	6495	12.0	4.92 × 10 <sup>9</sup>
	.1150	8969	4634	8.70	1.62 × 10 <sup>11</sup>
	.1716	8535	2878	5.83	5.15 × 10 <sup>12</sup>

The relation may be useful in some cases for calculating activities.

The osmotic pressures of these solutions will be dealt with in a later paper.

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### Discussion.

**Mr. J. L. Buchan** remarked that in the calculation of the activity of potassium chloride, a new standard state had been assumed. This was, he thought, to be deprecated in view of the confusion already existing, owing to the number of standard states which have been employed from time to time.

He suggested that the difficulty of integration, which this was designed to overcome, could be better dealt with by the method indicated in Lewis and Randall, "Thermo Dynamics," page 273 (1923).

**Dr. Perman** replied that he had spent much time and labour on the method indicated by Mr. Buchan, but he found (in the case of calcium chloride) that an accurate integration could not be made by its use.

# THE DISSOCIATION OF SODIUM SULPHATE DECA-HYDRATE.

By EDGAR PHILIP PERMAN AND WILLIAM DONALD URRY.

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## PART I. DISSOCIATION PRESSURE.

The dissociation pressure of salt hydrates has been studied by many investigators, but attention has been concentrated so far chiefly on methods of measurement rather than on obtaining complete data or on theoretical considerations.

The following work has been carried out with the object of investigating the free energy change associated with the formation of a salt hydrate over as wide a range as permitted by the stability of the compound. Sodium sulphate is well suited to this purpose. The dissociation pressure of the system decahydrate—anhydrous salt—vapour is high compared with that of other salt hydrate systems, and there is only one stable hydrate.

Schottky<sup>1</sup> has investigated some cases of this type, making thermal measurements as well as those of dissociation pressure, but the agreement between the two sets of results is not very close.

Bonnell and Jones<sup>2</sup> give a résumé of the methods used by numerous investigators. Our method was very similar to that of Bonnell and Jones, but was arrived at as a slight modification of that used by Downes and Perman,<sup>3</sup> the bubblers in the thermostat being replaced by a saturator containing the two forms of sodium sulphate. The saturator was made of two glass cylinders 29 cm. long and 4 cm. in diameter, connected at one end by a narrow glass tube; they were fixed in a horizontal position in the thermostat. The incoming air passed first through a drying and purifying train outside the thermostat, consisting of tubes containing soda-lime, lead acetate, and concentrated sulphuric acid respectively; it then passed through a narrow thin-walled tube (in the thermostat) containing copper turnings, to enable the air to take the temperature of the thermostat, and next into one end of the saturator. Coming out of the other end it passed through the 3-way mercury tap (see Downes and Perman).<sup>3</sup>

A saturator of different design was used in some of the experiments; it was 90 cm. in length and 1 cm. in diameter, but had a series of bulbs 2 cm. in diameter and 3 cm. apart. The two forms gave equally consistent results.

The mode of experiment was the same as described by Downes and Perman<sup>3</sup> except that the rate of aspiration was reduced to about one litre in 6 hours.

The results are put briefly in Table I. On plotting dissociation pressure against temperature, the results lie on a smooth curve.

<sup>1</sup> *Z. physikal. Chem.*, **64**, 415, 1908.

<sup>2</sup> *J. Chem. Soc.*, 321, 1926.

<sup>3</sup> *Trans. Far. Soc.*, **23**, 95, 1927.

TABLE I.

Temp. of Thermostat. (° C.).	Vol. of Air Aspirated (c.c. reduced to N.T.P.).	Weight of Water drawn off Grms.	Dissociation Pressure. Mm. of Hg.	Mean D.P.
17.5	4734	0.0592	11.54	
"	5729	.0715	11.58	11.56
20.0	5271	.0782	13.43	
"	5053	.0756	13.45	
"	3035	.0450	13.48	
"	5059	.0745	13.49	13.46
22.5	2841	.0490	15.97	
"	3987	.0684	15.99	
"	3463	.0597	16.03	16.00
25.0	3661	.0786	19.16	
"	3817	.0802	19.14	
"	4121	.0887	19.19	
"	3016	.0653	19.18	
"	3747	.0800	19.21	19.17
28.0	2752	.0709	23.30	
"	3095	.0951	23.15	
"	3782	.0980	23.25	23.23
30.0	1848	.0549	26.72	
"	1880	.0554	26.61	
"	2837	.0829	26.73	
"	2736	.0799	26.58	26.66
31.09	1948	.0621	28.77	
"	1881	.0598	28.92	
"	1875	.0595	28.85	28.85
31.91	1925	.0644	30.31	30.31

## Application of the Results.

(1) *The Free Energy Change Associated with the Hydration to Decahydrate.*

In the application of Nernst's theorem to determine the free energy from the total energy, it is necessary to consider a condensed system. Moreover the specific heat of ice varies normally with temperature. The free energy change was calculated therefore for the hydration by ice. Let  $\pi_0$  = the vapour pressure of the ice and  $\pi_\pi$  = the dissociation pressure. Then the maximum work or the free energy change  $A = RT \log_e \frac{\pi_0}{\pi_\pi}$  per mol. of ice. The vapour pressures of ice were calculated from the equation of Nernst<sup>4</sup> or Scheel.<sup>5</sup> In Table II. N. refers to Nernst's and S. to Scheel's

TABLE II.

Temp. ° C.	$\pi_0$	$\pi_\pi$	A per 10 Mols. of Ice.
0.0	4.58 (N.)	2.77	2732
15.0	14.73 (N.)	9.21	2689
20.0	21.16 (N.)	13.35	2683
22.5	25.25 (N.)	16.00	2680
25.0	30.08 (N.)	19.17	2670
27.5	35.11 (S.)	22.49	2661
30.0	41.47 (S.)	26.66	2661
32.0	47.29 (S.)	30.48	2663

<sup>4</sup> Vide Mellor's "Inorganic Chemistry," p. 435.<sup>5</sup> Verh. deut. physik. Ges., 8, 391, 1905.

equation. The dissociation pressures used at  $0^\circ$  and  $15^\circ$  are those of Baxter and Lansing.<sup>6</sup>

(2) *Dissociation Pressure and Heat of Dissociation.*

From the Kirchhoff relation between the heat of reaction at constant volume and the sum of the molecular heats of the participants,

$$\frac{dq}{dT} = A + BT + \dots$$

we get on integrating  $q = q_0 + AT + \frac{BT^2}{2} + \dots$

where  $q$  = the heat of dissociation at  $T^\circ$  absolute, and  $q_0$  = the heat of dissociation at absolute zero.

Substitute for  $q$  in the Clausius Clapeyron equation,

$$\frac{d \log_e \pi_\pi}{dT} = \frac{q}{RT^2} \text{ and integrate.}$$

Then  $\log_e \pi_\pi = -\frac{q_0}{RT} + \frac{A \log_e T}{R} + I + \dots$

Substituting values in the preceding table to evaluate  $q_0$ ,  $A$ , and  $I$ , the equation becomes

$$\log_{10} \pi_\pi = \frac{-60974.3}{2.30259 RT} - \frac{163.4738 \log_{10} T}{R} + 249.4969.$$

where  $R = 1.9875$  cals. and absolute zero =  $273.1$ .

TABLE III.—DISSOCIATION PRESSURE.

Temp. ° C.	Found.	Calculated.
20.0	13.35	13.35
22.5	16.00	16.06
25.0	19.17	19.18
27.5	22.49	22.69
30.0	26.66	26.67
32.0	30.48	30.14

The above equation is approximately that of a straight line, and  $\log \pi_\pi$  plotted against  $\frac{1}{T}$  will give a straight line. This has been shown to hold very closely.<sup>1</sup>

(3) *The Heat of Hydration by Liquid Water, Q.*

Using the previous notation, we have  $\frac{d \log_e \pi_\pi}{dT} = \frac{q}{RT^2} \dots (a)$ .

Similarly for water  $\frac{d \log_e \pi_0}{dT} = \frac{L}{RT^2} \dots (b)$ .<sup>7</sup>

<sup>6</sup> *J. Amer. Chem. Soc.*, 42, 419, 1920.

<sup>7</sup> See "Lectures on Theoretical and Physical Chemistry," Van't Hoff, Part I., p. 59.

Subtracting (a) from (b) we have  $\frac{d \log_e \frac{\pi_0}{\pi_\pi}}{dT} = \frac{L - q}{RT^2} \dots (c)$ .

But  $q = L + Q$ . Substituting in (c) and integrating,

$$\log_e \frac{\pi_0}{\pi_\pi} = \frac{Q}{RT} + c,$$

from which  $\log_{10} \frac{\pi'_0}{\pi'_\pi} - \log_{10} \frac{\pi''_0}{\pi''_\pi} = \frac{Q}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$ .

A value of Q has been worked out from the following data :—

0° C.  $\pi'_0 = 4.58$  mms.  $\pi''_0 = 2.77$  mms.  $Q = 1850$  cals. per mol. water.  
 22.5° C.  $\pi'_0 = 20.42$  mms.  $\pi''_0 = 16.00$  mms.

The value of  $dQ/dT$  is such that the Q/temperature graph is a straight line over the range 0° C. to 30° C. It is thus possible to extrapolate the results given in Part II. for the heat of hydration by liquid water. At 11.25° C. (the mean temperature of the previous calculation) Q, by direct measurement = 1829 cals. per mol.

## PART II. HEAT OF HYDRATION.

The heats of hydration of sodium sulphate have been determined at four temperatures between 20° C. and 30° C. As the work was carried out in the summer months of 1926, it was found impossible to work accurately at lower temperatures. The method of measuring the heat changes was identical with that used by Harrison and Perman.<sup>8</sup> When measuring the heat of solution, the salt weighed in a t.i. in walled tube was introduced into the water in the Dewar flask by pushing a glass plunger through the bottom of the tube. The following measurements were made :—

- (a) The Heat of solution (including the Heat of dilution) of 2.84 g. Na<sub>2</sub>SO<sub>4</sub> in 600.0 g. water.
- (b) The Heat of solution (including the Heat of dilution) of 6.44 g. Na<sub>2</sub>SO<sub>4</sub> less the heat of solution of  $\frac{1}{50} M$  Na<sub>2</sub>SO<sub>4</sub>, 10 H<sub>2</sub>O in 596.4 g. water.

The total quantity of water was the same in the two experiments and, since the saturated solutions were identical, the heat of dilution was the same in each case. Heat effect (a) – heat effect (b) gives the heat of solution of 1/50 mol. Na<sub>2</sub>SO<sub>4</sub>. 10 H<sub>2</sub>O, i.e., 1/50 of the heat of hydration. Owing to the large quantity of water used (600 g.) and the small quantity of salt (2.84 g. Na<sub>2</sub>SO<sub>4</sub>), it was assumed that the volume change was negligible.

The results in Table IV. were obtained. On plotting heat of hydration against temperature, the points lie on a straight line, and on extrapolation the value calculated from Van't Hoff's equation, and also Thomsen's value at 18° C., lie very close to it.

<sup>8</sup> Trans. Far. Soc., 23, 72, 1927.

TABLE IV.—HEAT OF HYDRATION OF SODIUM SULPHATE.

Temp. °C.	Heat Effect (a).	Mean.	Heat Effect (b).	Mean.	Heat of Hydration.
22.40	- 18.87 - 19.84 - 20.35 - 20.05	- 19.80	+ 379.7 + 380.2 + 382.2 + 381.9	+ 381.0	
24.90	- 30.35 - 30.42 - 29.70 - 29.84	- 30.08	+ 382.0 + 383.8 + 376.0 + 377.8	+ 379.9	- 20040
27.40	- 40.73 - 40.60 - 41.22 - 41.81	- 41.09	+ 377.2 + 377.5 + 378.7 + 379.0	+ 378.1	- 20499
29.90	- 55.57 - 54.79	- 55.18	+ 375.0 + 374.7 + 374.6	+ 374.8	- 20960
					- 21500

### The Application of the Nernst Heat Theorem to the Dissociation of a Salt Hydrate.

Let  $A$  = the free energy change,  $Q$  = the heat of reaction at constant volume (identical with the change in the internal or total energy), and  $Q_0 = Q$  at absolute zero.

Then Nernst's theory<sup>9</sup> requires that

$$A = Q_0 - \beta T^2 - \frac{cT^3}{2} - \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (1)$$

$$Q = Q_0 + \beta T^2 + cT^3 + \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (2)$$

These equations apply strictly only to solid systems, for they are based on the essential point of Nernst's theory, *viz.*, that as the absolute temperature is approached  $dA/dT$  approaches  $dQ/dT$  and becomes identical with it at temperatures near absolute zero. At these temperatures no liquid or gas can exist, and the test must therefore be made with quantities relating to the solid system only: Sodium sulphate—Ice—Sodium sulphate dehydrate.

In order to determine  $\beta$  it was more convenient to obtain a series of heats of hydration than to measure the specific heats of the participants, as is usually done. Such measurements of heats of hydration were therefore made and compared with heats calculated from values of  $A$  given in Part I., and the use of equations (1) and (2).

Having found  $Q_0$  and  $\beta$  in the equation  $A = Q_0 - \beta T^2$ ; by substituting in the equation  $Q = Q_0 + \beta T^2$  we obtain a value of  $Q$  at a given temperature  $T^0$  absolute. The heats of hydration have been measured at temperatures from 22.4° to 29.9°C. Taking the free energy change at 22.50°C. = 2680 cals. per 10 mols., and at 25.00°C. = 2670 cals., we get

$$A = 3269 - .00674T^2$$

$$Q = 3269 + .00674T^2.$$

<sup>9</sup> Nernst, "Applications of Thermodynamics to Chemistry," p. 50, 1907.

Column (3) in Table V. gives the heat of hydration by ice at the absolute temperature given in column (2). Column (4) gives the latent heat of fusion of ice, and on adding this to the heat of hydration by ice, we obtain the heat of hydration by liquid water. The experimental values are given in column (6). The agreement is as good as could be expected.

TABLE V.

Temp. °C.	Absolute Temp.	By Ice, Calas.	Latent Heat Fusion.	By Liquid (Calculated to nearest 5 cal.).	By Liquid (Found).
- 30.0	243.1	3667	11700	—	—
+ 5.0	278.1	3790	14850	—	—
18.0	291.1	3840	16020	19860	19220 Thomsen
22.4	295.5	3857	16416	20275	20040 P. and U.
24.9	298.0	3867	16641	20510	20499 "
27.4	300.5	3877	16866	20745	20960 "
29.9	303.0	3887	17091	20980	21500 "

### The Chemical Constant of Water Vapour.

Nernst has extended the application of his theorem to the case when vapour co-exists with any number of solid bodies. We then have<sup>10</sup>

$$\log_{10} K = - \frac{Q_0}{4.57T} + \Sigma n 1.75 \log_{10} T + \frac{\delta T}{4.57} + \Sigma n C,$$

where K is the reaction constant at constant pressure, Q<sub>0</sub> and δ having the same meaning as before.

$\Sigma n C$  = the algebraical sum of the chemical constants of the participants. The determination of the coefficient of T without an accurate knowledge of specific heats is uncertain, but the equation gives but slightly different results when this term is excluded.<sup>11</sup>

Considering the dissociation of a hydrate yielding vapour and anhydrous salt,  $\log_{10} K = \log_{10} \pi_\pi$  where  $\pi_\pi$  is measured in atmospheres.  $\Sigma n C$  is the chemical constant of one mol. of water vapour; Q<sub>0</sub> is obtained from the equation connecting dissociation pressure (in atmospheres) and heat of dissociation (Part I.).

$$\text{Then } C = \frac{12991}{4.57T} + \log_{10} \pi_\pi - 1.75 \log_{10} T.$$

Table VI. gives the values obtained.

TABLE VI.

Absolute Temp. °C.	$\pi_\pi$ (Atmos.).	C.	Mean.
273.1	0.00364	3.71	
288.1	.0121	3.65	
293.1	.0176	3.62	
295.6	.0210	3.62	
298.1	.0252	3.61	
303.1	.0351	3.58	

<sup>10</sup> Loc. cit., p. 97.

<sup>11</sup> Loc. cit., p. 101.

Nernst has deduced the chemical constant for water vapour to be 3·44 and 3·6 by different methods, but he employs throughout his applications the value 3·7 derived from the empirical formula,  $C = 1\cdot1a$ .<sup>12</sup> The apparent decrease of C with rising temperature is probably due to the exclusion of the term involving T. The final value of C is in better agreement with Nernst's values deduced from the experimental data than with that derived from the empirical formula.

<sup>12</sup> *Loc. cit.*, p. 75.

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## THE VAPOUR PRESSURES OF BINARY SYSTEMS.

By ALFRED W. PORTER, D.Sc., F.R.S.

(Received 13th April, 1928.)

It is well known that according to the law of Duhem-Margules if  $a_1$  be written for  $\pi_1/\Pi_1$  where  $\pi_1$  is the vapour pressure of one constituent in equilibrium with the system and  $\Pi_1$  the value when the second constituent is absent, and if similar symbols but with suffix 2 denote the similar quantities for the second constituent, then

$$\mu_1 \frac{\partial}{\partial \mu_1} \log a_1 = \mu_2 \frac{\partial}{\partial \mu_2} \log a_2$$

where  $\mu_1$   $\mu_2$  are the molar fractions of the constituents in the binary system each reckoned as of the same molecular type as in the vapour state.

This equation is not exact. It assumes that in the vapour state the vapours follow the law of perfect gases; also it neglects a term corresponding to very small changes in the volume of the system. Nevertheless, it is the most satisfactory general relation which is at present known.

The implication of this equation is that each side of the equation is the same symmetrical function of  $\mu_1$  and  $\mu_2$ .

This property restricts the choice of equations that can represent the variation of the vapour pressures with the concentration. Equations which have been assumed for this purpose in many cases violate this condition, and they should at once be rejected.

Possible values for each of the terms in the differential equation are

$$a, b\mu_1\mu_2, c\mu_1^2\mu_2^2, g\mu_1^3\mu_2^3, \text{etc.}$$

(arranged in order of complexity) where  $a, b, c, g$  are constants. It should be observed that in no case does a term represent peculiarities of a single constituent only. Each term, in fact, implies mutual action between the constituents and each constant belongs to both.

If  $e^{b_1}$  be written for  $a_1/\mu_1$  the values of  $\phi_1$  which correspond to the above terms are respectively

$$\begin{aligned} &\log \mu_1, (1 - \mu_1)^2, (1 - \mu_1)^3(1 + 3\mu_1), \\ &(1 - \mu_1)^4(1 + 4\mu_1 + 10\mu_1^2), (1 - \mu_1)^5(1 + 5\mu_1 + 15\mu_1^2 + 35\mu_1^3). \end{aligned}$$

These may be multiplied by any constants and may be taken singly, or together in any proportions. There is sufficient flexibility therefore in the selection of the constants to represent any experimental case.

The case  $\phi_1 = \beta(1 - \mu_1)^2$  has been often employed (by van Laar and others) and in a previous paper<sup>1</sup> I have developed certain general conclusions in regard to it. In the present paper I will deal with cases for which this particular term, by itself, is not adequate.

### Case I.—Aqueous Solution of Sugar.

The best data for the vapour pressures of water from such a solution

are those of  
Downes and  
Perman.<sup>2</sup>

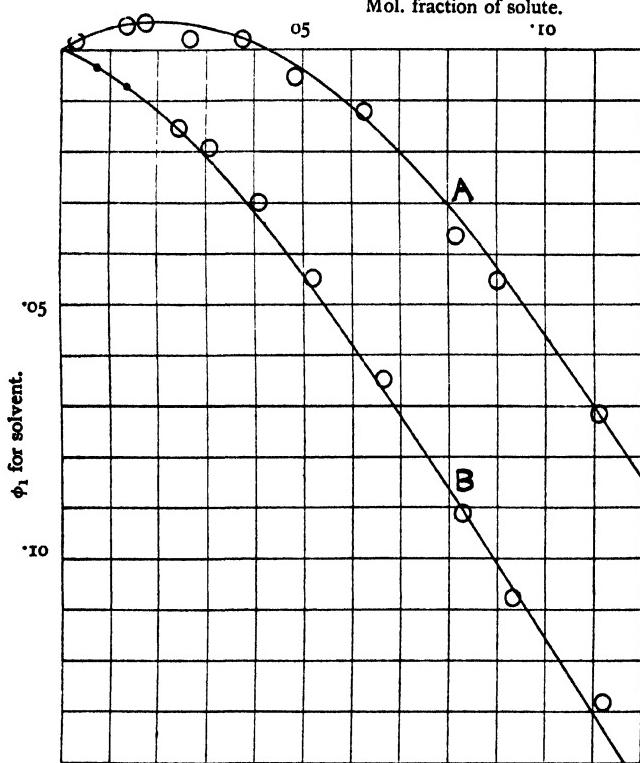


FIG. I.

$$\phi_1 = -4 \log \mu_1 - 10\mu_2^2.$$

Letting suffix one refer to the water and two to the sugar the data utilised and the values of  $\phi_1$  calculated are shown below for the temperature 80° C.

The values of  $\phi_1$  are plotted against  $\mu_2$  (i.e.  $1 - \mu_1$ ) in Fig. I. The small circles (curve A) are from the experimental data. Raoult's Law would require these values of  $\phi_1$  to be constant and equal to zero. The formula which satisfactorily represents these data is

$\mu_1$	$a_1$	$a_1/\mu_1$	$\phi_1$
.9959	.9972	1.001	+ .001
.9869	.9904	1.004	.004
.9825	.9871	1.005	.005
.9740	.9764	1.002	.002
.9616	.9626	1.001	+ .001
.9506	.9446	0.9937	- .006
.9371	.9249	0.9869	- .013
.9190	.8857	0.9638	- .037
.9103	.8689	0.9545	- .065
.8890	.8279	0.9313	- .071

This is a permissible form built up of the first two terms enumerated above. It will be seen that Raoult's law does not hold anywhere—not even in the most dilute region.

One advantage of obtaining a satisfactory equation for one constituent is that we can at once (owing to the Duhem-Margules relation) write down the similar expression for the second constituent, *viz.*

$$a_2 = \mu_2 \exp. [-'4 \log \mu_2 - 10(1 - \mu_2)^2].$$

### Case II.—Potassium Chloride Aqueous Solutions at 80° C.

The values given by Professor Perman<sup>3</sup> are quoted below with values of  $\phi_1$  deduced from them.

$\mu_1$ .	$a_1/\mu_1$ .	$\phi_1$ .
.9754	.9854	-.015
.9697	.9811	-.019
.9587	.9700	-.030
.9479	.9569	-.044
.9336	.9382	-.064
.9171	.9118	-.092
.9061	.8977	-.108
.8873	.8797	-.128

The values of  $\phi_1$  are plotted as circles on or about curve B (Fig. 1). The solid dots are obtained from extrapolated values of  $a_1$  given by Professor Perman. This extrapolation appears to be justified.

Since the curve starts out at an angle with the horizontal it is necessary to introduce a term  $\log \mu_1$  as in Case I. It was further found impossible to fit the values obtained from experiment satisfactorily without introducing two other terms. The equation finally selected and drawn as curve B (Fig. 1) is

$$\phi_1 = '4 \log \mu_1 - 12.41\mu_2^2 + 13.8\mu_2^3 (1 + 3\mu_1).$$

This equation is of a permissible form. Again, the corresponding equation for  $\phi_2$  is obtained by substituting  $\mu_2$  for  $\mu_1$  and vice versa, leaving the numerical coefficients unchanged.

The curve  $\phi_1$  presents such interesting peculiarities that I have calculated  $a_1$  from it not only for values of  $\mu_2$  from zero up to the saturation concentration of the solution *viz.* about .12 but for values ranging from  $\mu_2 = 0$  to  $\mu_2 = 1$ . This curve is shown in Fig. 2. *The same curve* also gives the values of  $a_2$ ; the abscissae being taken as values of  $\mu_1$  for  $a_1$  and as values of  $\mu_2$  for  $a_2$ . The ordinates  $a = 1$  determine points for which  $a_1$  (and also  $a_2$ ) has the same value as for the pure constituent.

Now a saturated solution (the point S on Fig. 2) which is necessarily in equilibrium with the pure solute must have the same value of  $a_2$  as the pure solute, *i.e.* it must have the value  $a_2 = 1$ . But saturation measurement shows that it occurs when  $\mu_2 = .12$  approximately. Thus the curve proves to be adequate, not only in the right-hand portion which is the portion actually fitted to experimental data, *but on the left-hand portion also.*

It may be urged that there is a second point, *viz.*  $\mu_2 = .55$  at which  $a_2 = 1$ . But this is in a region of instability. For at this point if a fortuitous escape of molecules of solute takes place it will, by the escape itself, increase the momentary value of  $a_2$  in the vapour region and

<sup>3</sup> This number, p. 334.

simultaneously diminish the value of  $\mu_2$  for the liquid. But the slope of the curve indicates that a diminution of  $\mu_2$  causes an increase in the equilibrium value of  $a_2$ ; hence more molecules escape and thus further diminish  $\mu_2$  and so on. The same argument applied to the point  $\mu_2 = .12$  shows that this value denotes a point of stability.

Further examination has shown me that another term is necessary in order to account for all the properties of the solution of KCl. This will be dealt with in a later paper.

We thus come across the remarkable fact that there are two stable regions separated by a region of instability. In one of these there is little

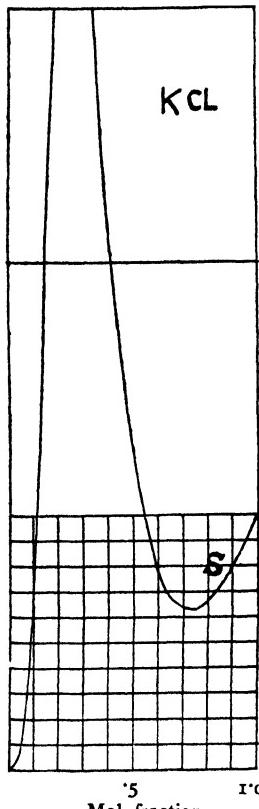


FIG. 2.

molecule and much solvent. This is the region

- 3 which is called solution. There is also a region in which there is much solute and very little solvent. The latter is commonly said to be absorbed; it is, in reality a dilute solution of "solvent" in a large amount of "solute."

- There are also special cases in which both solutions are fairly concentrated and both liquid—these are *immiscible* solutions. One of the phases may, however, possess considerable rigidity and the whole system is then a *colloidal* solution.

It is fairly well known that phosphoric anhydride can be so well dried that it fails to act as a drier. It is then in the absorption region. It can only absorb such a minute amount of water as to make  $a_1 = \text{unity}$ . It must be noted, however, that the equilibrium state can be set up only very slowly in the case where one of the phases is solid because it can penetrate inwards only by diffusion;—the action may take years to complete.

Returning now to the case of sugar. So far as the equation represents the facts there is no point at which  $a_2 = 1$ . This at least is consistent with the practical impossibility of crystallising sugar from its solution *under ordinary conditions*; but since it is crystallisable by evaporation *in vacuo* it is plain that in its case also an additional term is required similar to that which I have used for KCl. This small term can be neglected in calculating  $a_1$  for small values of  $\mu_2$  but it ultimately makes itself felt when  $\mu_2$  is nearly unity.

### Application to Reaction Equilibria.

It is now a well-recognised fact that a knowledge of the equilibrium vapour pressures of the constituents of any homogeneous reactive system enables an "equilibrium constant" to be obtained of the same form in terms of vapour pressures as that in which the masses enter in Guldberg and Waage's equation in the restricted case of perfect gas reactions. That is if  $\pi_1$ ,  $\pi_2$ , etc., are the vapour pressures in equilibrium with the system, and if in any small change that occurs, the number of molecules changes in the pro-

portions  $v_1 v_2$ , etc. (the molecules being taken as of the same complexity as in the vapour state), then  $\pi_1 v_1 \pi_2 v_2 \dots =$  a constant at constant temperature.

This equation is true so far as the vapours can be treated as perfect gases without any question arising as to the  $pV T$  relationships in the system itself.

This substitution of vapour pressures for masses (or molar fractions) leaves the problem of reactive equilibria unsolved because it gives no information as to what these vapour pressures will be. The vapour pressure equations developed in this paper are an attempt at supplying the lacking information. If for the sake of simplicity we take the case of two constituents only we may write some such expressions as

$$\pi_1 = \pi_1 \mu_1 e^{-\beta \mu_2^2}$$

and

$$\pi_2 = \pi_2 \mu_2 e^{-\beta \mu_1^2}$$

and the logarithm of the equilibrium constant becomes

$$v_1 \log \mu_1 + v_2 \log \mu_2 - v_1 \beta \mu_2^2 - v_2 \beta \mu_1^2.$$

If we endeavour to simplify matters by introducing factors,  $\kappa_1$ ,  $\kappa_2$ , so that

$$v_1 \log \kappa_1 \mu_1 + v_2 \log \kappa_2 \mu_2 = \text{constant}$$

the factors so introduced are the so-called activity coefficients. The object of this note is to emphasize that these factors

(1) are not constants but functions of the values of  $\mu_2$ ,  $\mu_1$ ,

(2) have values which depend not only upon the molar fraction which they multiply but are functions of the other substances present. This is indicated by the occurrence of  $\beta$  in both; for  $\beta$  is the coefficient of a term which represents mutual action between the components.

The values of these coefficients can be found only either by an experimental study of the vapour pressures of the actual system or by an experimental study of the reactions in the system itself. The values of the coefficients so found cannot in general be treated as constants, one for each component, but have values which vary for the same substance when the substances with which it is associated are changed.

Only in those cases in which the system is approximately an ideal gaseous system and for which therefore the value of  $\beta$  is very small does it seem likely that a rational simplification may become possible. In such cases the exponentials can be written.

$$1 - \beta \mu_2^2, \quad 1 - \beta \mu_1^2.$$

"Dilute" liquid systems are sometimes taken to have the same simplicity as imperfect gaseous systems. But it must be remembered that if the system is dilute in regard to one constituent it is very concentrated in regard to the other; in other words if  $\mu_2$  is small then  $\mu_1$  is large. In such cases it may be possible to write one exponential term as  $1 - \beta \mu_2^2$  but it is not possible to write the other in the same way. To express matters in another way, a solution may be nearly an "ideal liquid" for the solvent when the solute is present in small quantity only, but it is not nearly an ideal liquid from the point of view of the solute. [This is indicated by the lack of symmetry of such a curve as that in Fig. 2]. I do not think that this fact is generally understood.

I have illustrated these remarks by reference to a system of two components only. As the number increases the complications grow at an alarming rate. I have given some expressions for the vapour pressures in a ternary system in a previous paper.<sup>4</sup>

# THE EFFECT OF SUPERPOSED ALTERNATING CURRENT ON THE DEPOSITION OF ZINC-NICKEL ALLOYS.

BY HERBERT CHARLES COCKS.

Received 8th February, 1928.

The electrodeposition of nickel from aqueous solution is always accompanied to some extent by hydrogen discharge. For a constant current density, the current efficiency for nickel deposition increases as the ( $H'$ ) of the electrolyte decreases, and at a fixed ( $H'$ ), it increases with rise of current density within the range of 0·2 to 1·5 amps./dcm.<sup>2,1</sup>

The large polarisation which occurs during the deposition of nickel is due, mainly, to the irreversibility of its deposition and, to a less extent, to hydrogen overvoltage.<sup>2</sup> Both the reaction-resistance to nickel deposition and the hydrogen overvoltage increase with rise of current density and become smaller with rise of temperature. The increase of the reaction-resistance to nickel deposition with increase of current density causes a reduction in the current efficiency for the deposition of the metal with rise of current density, while the increase of hydrogen overvoltage with current density has the opposite effect.<sup>1</sup>

If an agent, such as superposed alternating current reduces both the reaction-resistance and the hydrogen overvoltage, its effect on the former will tend to cause an increase in the current efficiency for nickel while its action on the latter will tend to the reverse effect. In both cases, however, it should make the deposition potential less negative.

Zinc, on the other hand, is a metal which exhibits very little irreversibility of deposition, but for which the hydrogen overvoltage is high. The deposition of zinc from strongly acid solutions is dependent on the latter phenomenon.<sup>3</sup> Increase of temperature lowers hydrogen overvoltage and thus favours hydrogen evolution, while zinc deposition is favoured by high current density and a large metal ion concentration.<sup>2</sup> At a current density of 2·5 amps./dcm.<sup>2</sup>, the current efficiency for zinc only increases by about 2 per cent. with a change in  $p_H$  of the electrolyte of from 1 to 4.<sup>4</sup>

At a high temperature, and using solutions of identical metal ion and hydrogen ion concentrations, a low current density would be expected to favour the deposition of nickel relatively to that of zinc, whilst a high current density should have the opposite effect. This conclusion is confirmed by the results of experiments on the electrolysis of feebly acid solutions of mixtures of nickel and zinc sulphates.<sup>5</sup>

At low current densities the deposits consisted almost entirely of nickel and contained very little zinc, the cathode potentials approximating to the deposition potential of nickel. As the current density was raised, the zinc content of the deposit was found to increase very slowly, then, at a certain current density, it suddenly became greater than that of the nickel and the

<sup>1</sup> M. R. Thompson, *Trans. Amer. Electrochem. Soc.*, **41**, 349 (1922).

<sup>2</sup> Allmand and Ellingham, "The Principles of Applied Electrochemistry," p. 335.

<sup>3</sup> Tainton, *Trans. Amer. Electrochem. Soc.*, **41**, 388 (1922).

<sup>4</sup> Frölich, *Trans. Amer. Electrochem. Soc.*, **49**, 285 (1926).

<sup>5</sup> Foerster, *Elektrochemie wässriger Lösungen*, p. 375 (new edn.), *Z. Elektrochem.*, **22**, 96 (1916).

deposition potential approximated to that of zinc. Working at 80° C., with a solution of the composition, 0·5*N*. ZnSO<sub>4</sub>, 0·5*N*. NiSO<sub>4</sub>, 0·01*N*. H<sub>2</sub>SO<sub>4</sub>, the deposit contained 70-80 per cent. of nickel at a current density of 0·01 amps./cm.<sup>2</sup>,  $\epsilon_H$  being - 0·5 volt, while it contained 20-30 per cent. of nickel at 0·02 amps./cm.<sup>2</sup>,  $\epsilon_H$  then being about - 0·7 volt.

The effect of superposed A.C. on the deposition of nickel has been investigated by Kohschütter and Schödl,<sup>6</sup> who found that the polarisation observed during deposition with D.C. alone was greatly reduced but not to zero. The effect was larger the greater the ratio A.C. : D.C. They found no increase in the current efficiency for nickel deposition when low ratios were used, but a decrease with high ratios. Isgarischew and Berkmann,<sup>7</sup> have studied the effect of superposed A.C. on the polarisation curves for nickel deposition. With a solution of NiSO<sub>4</sub> of very low (H'), A.C. of 50 cycles had very little effect. When the D.C. was kept constant and the A.C. was gradually increased during deposition from a solution of nickel ammonium sulphate of higher (H'), they found that the polarisation first increased, passed through a maximum, and then decreased. Under the same conditions the polarisation was always decreased when a solution of much higher (H'), viz., *N*. NiSO<sub>4</sub>, 0·1*N*. H<sub>2</sub>SO<sub>4</sub>, was used. They came to the conclusion that the chief effect of A.C. was on the hydrogen discharge accompanying the metal deposition. They attributed the increase of polarisation to a greater difficulty of hydrogen discharge during the cathodic pulses of the current and the reduction of polarisation to the depolarising action of oxygen liberated by the reverse current.

Hydrogen overvoltage is considerably reduced by the superposition of A.C. Goodwin and Knobel,<sup>8</sup> observed that, with a sufficiently large ratio of A.C. : D.C., hydrogen was evolved at average potentials more positive than the reversible value. Here, also, the depolarising effect of oxygen liberated during the anodic pulses of the current is considered to be the cause of the reduction of the irreversibility of the electrode process.<sup>9</sup>

The small polarisation observed in zinc deposition is also reduced by the superposition of A.C. The decrease of the polarisation has been ascribed to a reduction in the concentration of atomic hydrogen on the surface layer of the cathode.<sup>10</sup>

The work described in this paper is an investigation of the effect of superposed A.C. in a case where Zn<sup>2+</sup>, Ni<sup>2+</sup> and H<sup>+</sup> are discharged simultaneously, i.e., the deposition of the alloy zinc-nickel.

### Experimental.

Experiments were first carried out with the electrolyte 0·5*N*. ZnSO<sub>4</sub>, 0·5*N*. NiSO<sub>4</sub>, 0·01*N*. H<sub>2</sub>SO<sub>4</sub>, at 80° C., using D.C. only, but although evidence of a break in the composition-current density curve was obtained, the results did not seem to be reproducible. Indications were obtained that the deposits were not wholly metallic. (If, during the deposition of zinc or nickel, the (H') of the electrolyte adjacent to the cathode becomes too low, hydroxide tends—at least at ordinary temperatures—to become included in the deposit.) It was found that a similar electrolyte containing ammonium sulphate gave more reproducible results.

About  $\frac{1}{3}$  litre of the electrolyte, 0·5*N*. ZnSO<sub>4</sub>, 0·5*N*. NiSO<sub>4</sub>,

<sup>6</sup> *Helv. Chim. Acta*, 5, 593 (1922).

<sup>7</sup> *Z. Elektrochem.*, 31, 180 (1925).

<sup>8</sup> *Trans. Amer. Electrochem. Soc.*, 37, 617 (1920).

<sup>9</sup> But see Jones, *ibid.*, 41, 151 (1922).

<sup>10</sup> Allmand and Cocks, *Proc. Roy. Soc.*, A, 112, 259 (1926).

$0.5N.$   $(\text{NH}_4)_2\text{SO}_4$ ,  $0.01N.$   $\text{H}_2\text{SO}_4$ , was used for each experiment. It was maintained at  $80 \pm 1^\circ \text{C}.$ , in a beaker which served as electrolysis vessel. The platinum cathode, to which a platinum wire was welded, had a total area of  $35.6 \text{ cms.}^2$ . In the experiments in which the composition of the alloy was determined, both sides of the cathode were used and it was suspended by means of the wire from a terminal which passed through a support fitted on the beaker. The cathode could thus be removed conveniently for weighing. The deposits were dried at  $110^\circ \text{ C.}$  to constant weight and the nickel was determined gravimetrically by means of dimethyl glyoxime. Two zinc and two nickel anodes, placed in small porous pots filled with solutions of the respective sulphates, were used. They were all connected electrically and disposed symmetrically around the cathode. By this means, at least some of each metal which left the solution was replaced and the current should have been fairly evenly distributed at the cathode.

Only about  $0.2$  to  $0.4 \text{ g.}$  of alloy was deposited in each experiment and the electrolyte was very frequently replaced by an unused portion.

The alternating current was obtained from a 16-pole alternator. With the arrangement shown (Fig. 1), although a leak of *A.C.* into the *D.C.* part

of the circuit and *vice versa* occurs, the readings of the hot-wire and moving-coil ammeters in series with the cathode only indicate the current which passes through the electrolysis cell. The moving-coil instrument gives the value of the *D.C.* only, while the reading of the hot-wire ammeter is the square root of the sum of the squares of the *A.C.* (in r.m.s. amperes) and the *D.C.*

In the experiments in which the average cathode potential was measured, the wire on the cathode was sealed into a glass tube and

connection made by mercury. Only one side of the cathode was used, the back being insulated by baked shellac varnish: it was also pressed up against a glass plate. These changes were made so that a Luggin tube could be pressed up against the cathode and so that a good electrical connection could be made to the latter. The electrical connections were similar to those shown in Fig. 1, but only one zinc and one nickel anode were used and a lead was taken directly from the cathode to the potentiometer. One end of the Luggin tube was pressed against the cathode and the other dipped into cold electrolyte contained in a small vessel. This was connected (just before taking readings), by an inverted U-tube filled with the solutions, to another small vessel filled with  $3N.$  KCl. Into the latter dipped the side-tube of a normal calomel electrode. The purpose of this arrangement was to prevent diffusion of the hot electrolyte into the  $3N.$  KCl, and to avoid a junction of a hot electrolyte with a cold, dissimilar one.

In all cases the alloy deposited in one experiment was dissolved off the cathode before it was used for the next. The volume of the electrolyte was always maintained by the addition of hot water. Throughout all the experiments small quantities of  $N.$   $\text{H}_2\text{SO}_4$  were added at intervals of 5 or 10 mins., the quantity added being that estimated to maintain the acidity at  $0.01N.$  In some cases this was successful but in others it was not. In

Moving Coil Ammeter. Hot Wire Ammeter.

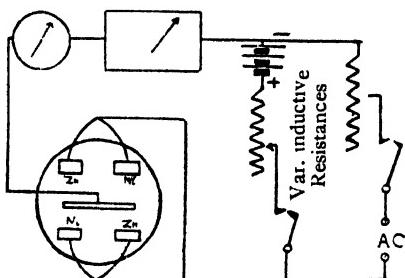


FIG. 1.

extreme cases the acidity at the end of an electrolysis was found to be  $0.02N$ , or had dropped to zero as estimated by titration using congo red as

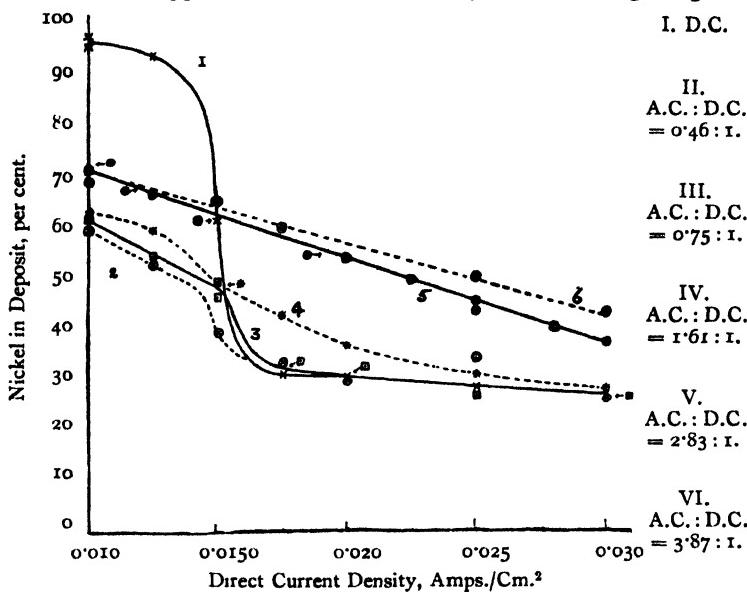


FIG. 2.

indicator. It would, no doubt, have been much better to have used a well-buffered electrolyte similar to that employed by Glasstone and Symes in their work on the electrodeposition of iron-nickel alloys.<sup>11</sup> The electrolyte was well stirred in all experiments.

The visual phenomena observed during electrolysis may now be briefly described. When the currents were first switched on, the cathode became completely covered with bubbles and then hydrogen was evolved in quantities which varied according to the *D.C.* density and the

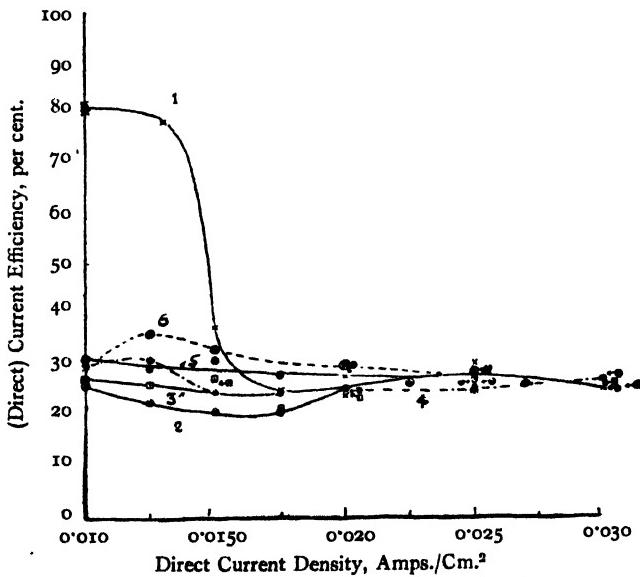


FIG. 3.—NICKEL (Curves I.-VI. as in Fig. 2).

<sup>11</sup> *Trans. Farad. Soc.*, 23, 213 (1927).

ratio  $A.C. : D.C.$ . Usually the number of bubbles which adhered to the cathode gradually decreased as the experiment proceeded; in a few cases, none remained at the end. It is of interest that in one case (composition experiment,  $D.C.$  only,  $0.02$  amps./cm.<sup>2</sup>) the deposit appeared to be quite

bright during the first 20 mins. of the electrolysis and then suddenly became dull-white and remained so. As a rule, the deposits obtained at potentials below  $-0.7$  volt (*i.e.*, below a  $D.C.$  density of  $0.02$  amps./cm.<sup>2</sup>, for  $D.C.$  alone and for  $A.C. : D.C.$  =  $0.46 : 1$ ,  $0.75 : 1$ , and  $1.61 : 1$ , and in all cases for  $A.C. : D.C. = 2.83 : 1$  and  $3.87 : 1$ ) were bright, or, in a few cases, light grey. Those obtained above  $-0.7$  volt were usually dull-white.

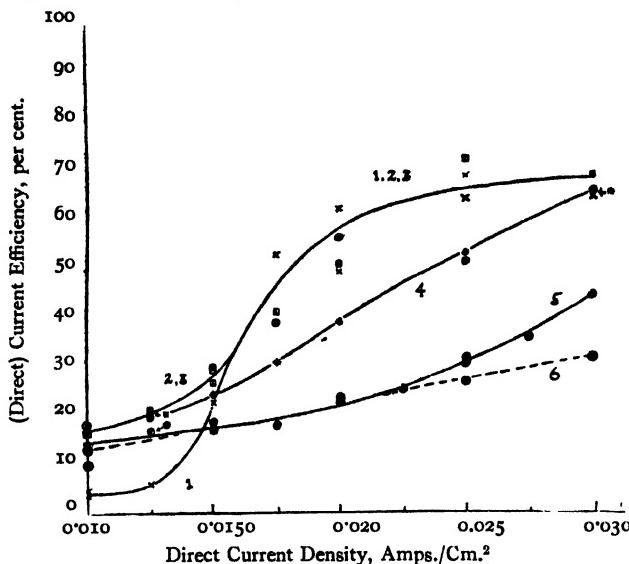


FIG. 4.—ZINC (Curves I.-VI. as in Fig. 2.)

$2.83 : 1$  and  $3.87 : 1$ ) were bright, or, in a few cases, light grey. Those obtained above  $-0.7$  volt were usually dull-white.

### Results of Current Efficiency Experiments.

The results for  $D.C.$  and for a superposed  $A.C.$  of 40 to 50 cycles per sec., are given graphically in Figs. 2 to 6. The percentage current efficiencies are calculated on the basis of the  $D.C.$  component of the current as measured by the moving-coil meter. Those for nickel are calculated from the weight of nickel determined by analysis and those for zinc from the weight of zinc obtained by subtracting the weight of nickel from the total weight of the deposit. It is recognised, however, that the deposits probably contained traces of

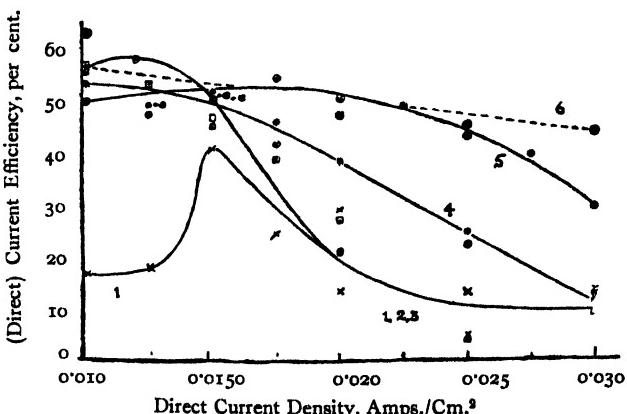


FIG. 5.—HYDROGEN (Curves I.-VI. as in Fig. 2.).

hydroxide. The difference between the sum of the percentage current efficiencies for nickel and zinc thus arrived at and 100 is taken as that for hydrogen.

### Deposition Potentials.

The current was allowed to flow from 15 to 30 mins. (according to the current density) before the first reading of the average cathode potential was taken. Then seven readings were taken at intervals of 5 mins. The potentials given below, all of which are on the hydrogen scale, are each the mean of these seven readings. In some cases the potentials measured during the  $\frac{1}{2}$  hour were constant but in other cases they varied. The frequency was from 40 to 50 cycles per sec., and the temperature  $80 \pm 1^\circ\text{C}$ . in all cases. The results are shown graphically in Fig. 6. Only one curve is drawn for A.C.:D.C. = 0.46 : 1 and 0.75 : 1, as the points lie close together.

As an example of an experiment in which the readings were very constant, one in which D.C. only was used, at a density of 0.025 a mps./cm.<sup>2</sup>, may be given:

here the potential only varied from -0.775 to -0.773 volt. As one in which they were variable, the experiment in which the D.C. density was 0.0125 amps./cm.<sup>2</sup>, and the ratio of A.C.:D.C. was 0.75 : 1 where the potential varied from -0.593 to -0.559 volt, may be taken.

The following experiments were made in order to try to confirm the small differences in potential (indicated by the curves in Fig. 6), observed with the different A.C.:D.C. ratios at low D.C. densities and with ratios of 1.61 : 1 and under at D.C. densities approaching 0.03 amps./cm.<sup>2</sup>. In these experiments the deposit was not removed from the cathode between the various steps.

(a) *Electrolyte, 0.5 N. NiSO<sub>4</sub>, 0.5 N. ZnSO<sub>4</sub>, 0.5 N. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 0.01 N. H<sub>2</sub>SO<sub>4</sub>.*

*A.C.:D.C., 0 : 1, 0.46 : 1 etc., to 3.87 : 1.*

*D.C. density, 0.010 amps./cm.<sup>2</sup>.*

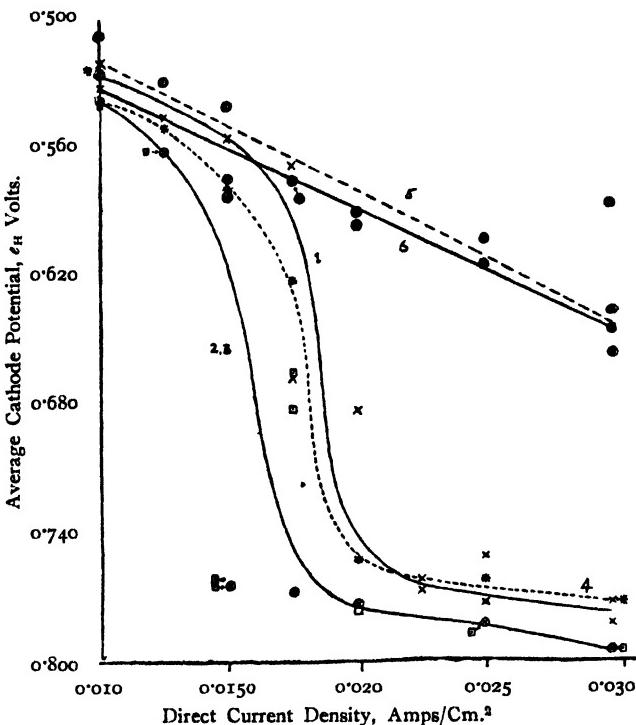


FIG. 6 (Curves I.-VI. as in Fig. 2).

## DEPOSITION OF ZINC-NICKEL ALLOYS

Direct Current Density, amps./cm. <sup>2</sup>	D.C. only.	Ratio A.C. : D.C.				
		0·46 : 1.	0·75 : 1.	1·61 : 1.	2·83 : 1.	3·87 : 1.
0·010	- 0·520	- 0·537	- 0·540	- 0·538	- 0·526	- 0·530
'0·010	'531	'539	—	—	'507	—
'0·125	'546	'562	'561	'551	'547	—
'0·125	—	—	—	—	'529	—
'0·125	—	—	—	—	'528	—
'0·15	'555	'765	'765	'579	'583	'574
'0·15	—	—	'762	—	'540	—
'0·175	'568	'768	'682	'622	'575	'576
'0·175	'668	—	'665	—	—	—
'0·20	'683	'774	'777	'753	'595	'590
'0·225	'767	—	—	—	—	—
'0·225	'762	—	—	—	—	—
'0·25	'774	'783	'784	'762	'602	'614
'0·25	'773	—	—	—	—	—
'0·25	'751	—	—	—	—	—
'0·30	'773	- 0·795	- 0·796	- 0·773	'585	- 0·644
'0·30	- 0·783	—	—	—	'635	—
0·030	—	—	—	—	- 0·655	—

With D.C. only the potentials were :—

$$\begin{array}{ll} \text{after } 5 \text{ mins.} & - 0\cdot522 \text{ volt } e_H \\ \text{, } 10 \text{ " } & '524 \text{ " } \\ \text{, } 15 \text{ " } & '526 \text{ " } \end{array}$$

The A.C. was then superposed for 15 mins. at each ratio and readings taken at 5 min. intervals. No definite change in potential could be observed at any ratio—the potential only fluctuated about the mean value of - 0·524 volt. The extreme values were observed with A.C. : D.C. = 0·46 : 1, these being - 0·518 volt after 5 mins., and - 0·534 volt after 10 mins. After the A.C. had been switched off for 15 mins., the D.C. potential was - 0·525 volt.

(b) *Electrolyte, N. NiSO<sub>4</sub>, 0·5 N. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 0·01 N. H<sub>2</sub>SO<sub>4</sub>. D.C. density, 0·01 amps./cm.<sup>2</sup>.*

Readings were taken at 5 min. intervals at each ratio. In experiment (1) the potentials became more positive by about 5 millivolts during the 15 mins. for each ratio, but in (2) they did not—they more or less varied about a mean value. In (1) the ratios were altered in the order 0·46 : 1, 1·61 : 1, 0·75 : 1, but in (2) they were changed in the order shown below :—

A.C. : D.C.	Change from mean initial D.C. value.
0·46 : 1	(1) + 13 millivolts.
0·75 : 1	+ 42 ,,
1·61 : 1	+ 75 ,,
0·46 : 1	(2) + 9 ,,
0·75 : 1	+ 23 ,,
1·61 : 1	+ 85 ,,
Mean initial D.C. value	(1) - 0·505 volt.
" final " "	- 0·473 ,,
Mean initial D.C. value	(2) - 0·502 ,,
" final " "	- 0·481 ,,

These results under (b) agree qualitatively with those of Isgarischew and Berkmann<sup>7</sup> for the electrolyte  $N\cdot NiSO_4$ ,  $0\cdot1 N\cdot H_2SO_4$ . The superposed current has a depolarising action.

- (c) *Electrolyte,  $N\cdot ZnSO_4$ ,  $0\cdot5 N\cdot (NH_4)_2SO_4$ ,  $0\cdot01 N\cdot H_2SO_4$ . D.C. density,  $0\cdot03$  amps./cm.<sup>2</sup>*

Here the cathode potential more or less varied about a mean value during the 15 mins. for each ratio.

<i>A.C. : D.C.</i>	<i>Change from mean initial D.C. value.</i>
$0\cdot46 : 1$	- 2 millivolts.
$0\cdot75 : 1$	+ 1 "
$1\cdot61 : 1$	+ 9 "
Mean initial <i>D.C.</i> value	- $0\cdot839$ volt.
" final " "	- $0\cdot828$ "

The contrast between the results under (b) and (c) and those for the mixed electrolyte, under (a), is interesting.

### Discussion.

With regard to the results with *D.C.* alone, attention is directed to the large increase in the current efficiency for hydrogen at the "critical current density" of about  $0\cdot015$  amps./cm.<sup>2</sup>. It appears that, as the current density is raised, the reaction-resistance to nickel deposition is increased and hydrogen evolution becomes greater. Then, as the current density is still further increased, the hydrogen overvoltage rises and zinc deposition is proportionately increased until it becomes the main process.

The explanation which will be given of the influence of superposed *A.C.* on the deposition of the alloy is based upon:—

(a) The known depolarising effect of the superposed current on irreversible electrode processes when its strength relative to that of the *D.C.* component is such that reverse current flows.

(b) An assumption as to the nett result of the periodic increases of current density above that of the *D.C.* component. This assumption is primarily made *ad hoc* in respect of the present phenomena. It may, perhaps however apply to other cases in which there is a sudden change in the electrode process with a small change of current density.

The data for *A.C. : D.C.* =  $0\cdot46 : 1$ , where the current is a pulsating direct one, will be considered first. It is upon the results obtained with this current, rather than with *D.C.* alone, that the elucidation of those obtained with other ratios of *A.C. : D.C.* is based. When the *D.C.* density is  $0\cdot01$  amps./cm.<sup>2</sup>, the current density at the minima of the pulses is  $0\cdot004$  amps./cm.<sup>2</sup>, and that at the maxima  $0\cdot016$  amps./cm.<sup>2</sup>. At the "critical direct current density" of  $0\cdot015$  amps./cm.<sup>2</sup>, the cathode process is in a state of instability. It is assumed that the periodic rise of current density above this critical value when pulsating current of *D.C.* component  $0\cdot01$  amps./cm.<sup>2</sup> is used, results in the production of a state of affairs similar to that due to an unvarying *D.C.* at a density of  $0\cdot016$  amps./cm.<sup>2</sup>, but that the cyclic decreases of current density below the "critical current density" do not cause a return to the conditions obtaining below the latter value.

If the conditions with the pulsating current were the same as when using a *D.C.* density of  $0\cdot016$  amps./cm.<sup>2</sup>, the current efficiency for nickel would be reduced from 79 to 28 per cent., that for zinc would be increased

from 4 to 33 per cent. and that for hydrogen raised from 17 to 37 per cent. The observed current efficiencies with pulsating current were:—Ni 26 per cent., Zn 17 per cent. and H<sub>2</sub> 57 per cent. There is thus some hydrogen evolution at the expense of zinc deposition, hence the percentage of nickel in the deposit is greater than that obtained with an unvarying *D.C.* of 0.016 amps./cm.<sup>2</sup>

As the density of the *D.C.* component of the pulsating current is increased, still keeping the same *A.C.* : *D.C.* ratio, the conditions become more and more like those for steady *D.C.* densities above 0.015 amps./cm.<sup>2</sup>, and when the *D.C.* component is at a density above the "critical value," the periodic variation of current density has no longer an appreciable effect. The current efficiency for nickel is hardly affected by a further increase of steady *D.C.* density, hence pulsating current gives the same current efficiency for nickel as the unvarying current. For zinc, the current efficiency rises according to the value of the density of the *D.C.* component in almost complete agreement with its rise with the density of *D.C.* alone. (Only one curve is drawn in Fig. 4 for *D.C.* alone, *A.C.* : *D.C.* = 0.46 : 1 and 0.75 : 1.) That for hydrogen decreases in a similar manner. (Only one curve is drawn for the three currents in Fig. 5.) It follows, therefore, that above the "critical direct current density," the composition of the deposits obtained with pulsating current follows the curve for *D.C.* alone (Fig. 2).

The slight increase in polarisation above the *D.C.* value, observed with *A.C.* : *D.C.* = 0.46 : 1 and 0.75 : 1 (see Fig. 6; one curve is drawn for both ratios), below the "critical current density" is qualitatively in agreement with the higher current efficiency for zinc, but there is no apparent reason for the slight increase observed above the "critical current density."

As the strength of the *A.C.* relative to the *D.C.* is increased, the periodic increases of current density at the maxima occur in greater degree. In the case of *A.C.* : *D.C.* = 2.83 : 1 and 3.87 : 1, the *average* current density at the cathodic pulses is always above the "critical current density," hence the assumption made under (b) above, is even more justified. When *A.C.* : *D.C.* > 1/√2 : 1, i.e., > 0.707 : 1, the depolarising effect of *A.C.* (see (a) above) will take place. This is attributed, as has been done by other investigators, to oxygen discharge during the anodic pulses of the current. As was mentioned above, it has been shown that superposed *A.C.* largely reduces the polarisation for nickel deposition, that with a sufficiently high ratio of *A.C.* : *D.C.*, it completely eliminates hydrogen overvoltage, and that it has a slight depolarising effect in zinc deposition.

In the deposition of the alloy, when *A.C.* : *D.C.* = 0.75 : 1, there is a slight depolarising effect due to the small anodic pulses. When the *D.C.* component has a density of 0.01 amps./cm.<sup>2</sup>, the current efficiency for nickel is slightly increased above that for *A.C.* : *D.C.* = 0.46 : 1 while the zinc and hydrogen current efficiencies are barely affected (see Figs. 4 and 5; one curve is drawn for *A.C.* : *D.C.* = 0.46 : 1 and 0.75 : 1). The deposit thus contains a little more nickel than with *A.C.* : *D.C.* = 0.46 : 1 but on account of effect (b) above, less nickel than with *D.C.* alone. Above the "critical current density," zinc deposition is the main process, hence the effect of the slight depolarising action of the anodic pulses is inappreciable. The composition of the alloy thus almost follows the *D.C.* curve.

With *A.C.* : *D.C.* = 2.83 : 1, the depolarising effect is much greater than with *A.C.* : *D.C.* = 0.75 : 1 and the retardation to nickel deposition is slightly reduced, especially below the "critical current density," where hydrogen overvoltage is low. Above the "critical current density," hydrogen overvoltage which with *A.C.* : *D.C.* = 0.75 : 1 was high, is de-

polarised and hence the current efficiency for hydrogen is increased and that for zinc decreased. The percentage of nickel in the deposit is thus greater than with  $A.C. : D.C. = 0.75 : 1$  both below and above the "critical current density."

The results for  $A.C. : D.C. = 1.61 : 1$  are intermediate between those for  $A.C. : D.C. = 0.75 : 1$  and  $2.83 : 1$ . At  $A.C. : D.C. = 2.83 : 1$ , the depolarising effect of  $A.C.$  has apparently almost reached its limit, hence a further increase of  $A.C.$ , i.e. when  $A.C. : D.C. = 3.87 : 1$  only results in a slightly greater depolarisation, which is, however, distinctly noticeable when the density of the  $D.C.$  component is above about  $0.025$  amps./cm.<sup>2</sup>

The deposition potential-current density curves (Fig. 6) indicate a slight increase of polarisation for a change of  $A.C. : D.C.$  of from  $2.83 : 1$  to  $3.87 : 1$ . This may be due to experimental error. It will be noticed however, that while the composition-current density curves for these two ratios diverge as the density of the  $D.C.$  component is increased, those for the deposition potential-current density, converge.

A comparison of the curves in Fig. 2 with those in Fig. 6, will show that alloys of the same composition have been produced at different deposition potentials according to the type and strength of the current used in their deposition, e.g., the potential of the alloy deposited at a  $D.C.$  density of  $0.02$  amps./cm.<sup>2</sup>, with  $A.C. : D.C. = 1.61 : 1$  is about  $0.1$  volt more negative than that of the one deposited at a  $D.C.$  density of  $0.03$  amps./cm.<sup>2</sup>, with  $A.C. : D.C. = 2.83 : 1$ , although both had the composition, Ni 36 per cent., Zn 64 per cent. The alloy deposited at the more negative potential was dull-white while the other was mainly bright.

Before concluding, it may be mentioned that three experiments were made with superposed  $A.C.$  of higher frequency with the following results:

FREQUENCY 400-450 CYCLES/SEC.  $A.C. : D.C. = 2.83 : 1$ .

D.C. Density amps./cm <sup>2</sup> .	Wt. of Nickel in Deposit, Per Cent.	Current Efficiencies, Per Cent.	
		Ni.	Zn.
0.010	60.3	32.8	19.4
0.020	33.8	23.5	41.4
0.030	27.1	26.4	64.5

Goodwin and Knobel,<sup>8</sup> working between the limits of 2 and 100 cycles/sec., found that the effect of  $A.C.$  in reducing hydrogen overvoltage fell off with rise of frequency. The depolarising effect is less at 430 than at 43 cycles/sec., in the case of the deposition of nickel alone (Unpublished results of the Author), while the effect of  $A.C.$  on the polarisation for zinc deposition is hardly affected by a change of frequency of from 50 to 450 cycles/sec. (Allmand and Cocks).<sup>10</sup> As a consequence of these observations, the results for the deposition of the alloy with superposed  $A.C.$  of 400 to 450 cycles appear to fall into line if it is assumed that the results for  $A.C. : D.C. = 0.46 : 1$  at 400 to 450 cycles are the same as those at 40 to 50 cycles. As the data for this ratio at the higher frequency are not available, the effect of frequency will not be discussed further.

The Author wishes to express his thanks to Professor A. J. Allmand for suggesting this investigation and for his help and interest in all stages of the work. His thanks are also due to Mr. R. H. D. Barklie, M.Sc., for

suggestions which led to the development of the explanation of the results.

### Summary.

- (1) An outline of the phenomena attending the cathodic deposition of zinc and nickel separately and together is given.
- (2) An investigation of the deposition of the alloy, zinc-nickel from an acid sulphate electrolyte using *D.C.* and superposed *A.C.* is described.
- (3) The variation of composition of the alloy and the average deposition potential with *D.C.* density and the ratio *A.C. : D.C.* is recorded.
- (4) The results are discussed, and an explanation of the effect of superposed *A.C.* is given, based upon:—
  - (a) The known depolarising action of the superposed current on irreversible electrode processes.
  - (b) The assumed nett result of the periodic increases of current density above that of the *D.C.* component.

*University of London,  
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**The Free Energy of Transition in the System Calcite-Aragonite. The Free Energies of Solid Compounds deduced from their Crystal Structure with special reference to Calcite and Aragonite.** By J. L. BUCHAN. (Vol. 23, pp. 666 and 672.)

*(Read before the Society on 29th February, 1928.)*

### DISCUSSION.

**The Author** in presenting the papers mentioned that on page 669 the equation for converting *E.M.F.* into free energy should be

$$F = 3 \times E \times 23,070 \text{ cals. per g. mol.}$$

which in turn gave the free energy of transition of aragonite into calcite as  $- 620$  cals. per g. mol. instead of  $- 414$  cals. per g. mol. as stated on page 671. He was indebted to H. Backström for calling attention to the errors.

**Professor F. G. Tryhorn** said that the small difference between the free energies of calcite and aragonite at ordinary temperatures might perhaps account for the power which some marine organisms appeared to possess of depositing calcium carbonate in the form of aragonite, in an environment in which calcite would seem to be the stable phase. It might be that, if the deposition of this substance through a membrane occurred with a moderately high velocity, the molecules which broke away first from the adsorbed layer were those of the highest energy content, which gave rise therefore to the aragonite phase.

**The President** raised the question, arising out of the second paper, how far it was legitimate to make use of a dielectric constant in such cases. The dielectric constant was essentially a property of matter in the mass; when dealing with the forces between two adjacent ions it seemed incredible that there could be any property which could be considered as even approximately constant over such a short range, in rapidly varying fields of force. That consideration made the use of such formulæ as that used by the

author very hazardous, and he would like to ask how far the conclusions could be considered as independent of any assumptions concerning the dielectric constant. He also asked whether it had been determined under what conditions aragonite would change spontaneously into calcite, seeing that the former mineral could exist through geological ages. Was contact with a solvent common to the two minerals essential?

**Professor Lowry** remarked that in the case of more soluble materials the difficulty was to maintain a supply of small particles to saturate the solution; their persistence in the case of calcite was presumably due to the very small solubility of the crystals in water saturated with carbon dioxide.

**Professor Allmand** asked Mr. Buchan if he would state more fully the reason for regarding the value calculated from Kohlrausch's results as unreliable.

**The Author** in reply said that with regard to the President's question, it seemed to him reasonable to speak of a dielectric constant when only two ions are considered, for the following reasons. Although the dielectric constant as ordinarily measured was a property of matter in bulk, it should be the average of the values obtained if the pairs of ions making up the bulk were examined separately. Therefore, although the free energy calculated by this method might not be strictly true for any particular ionic pair, it was an average value, for which a true value for one g. mol. could be calculated. Dielectric constants were used in a similar way when calculating internal fields in liquids.

For aragonite to change spontaneously into calcite, the conditions were not known so far as he was aware. Such changes did take place, as in coral reefs and in certain fossils, and in these cases a common solvent would be present. The change, however, was very slow, and in his experiments the author found no evidence of any transformation of the material in his electrode vessels.

In reply to Professor Lowry's remark about the persistence of small particles in the calcite this might certainly be due to the low solubility of calcium carbonate, but this particular case was complicated by the pulverising action of the bubbles of gas which passed through the solution and kept the solid in suspension. This would tend to maintain the supply of small particles.

The reasons for regarding the values obtained from Kohlrausch's results as unreliable have been dealt with by H. Backström.<sup>1</sup>

<sup>1</sup> *Z. physik. Chem.*, 97, 219-220, 1920.

#### REVIEWS OF BOOKS.

**Preparation of Scientific and Technical Papers.** By PROFESSOR S. F. TRELEASE and E. S. YULE. (London, 1927: Bailliere, Tindall & Cox. Pp. 117. Price 7s. net.)

Everyone concerned with the publications of a Scientific Society will agree that there is ample need for a book such as the authors now put forward. Papers are frequently submitted for publication in very untidy form and with diagrams which cannot be reproduced. The papers, moreover, too often betray a lack of critical revision or a failure to appreciate that the light of good work should not be hidden beneath the bushel of verbose irrelevance.

The subject is treated adequately by the authors, and there is little information required by those preparing papers for publication which is not to be found within its covers.

If all the advice in this book were taken the work of editing a Journal such as these Transactions would be very considerably lightened. In view of the fact that the authors hold academic positions in America, it will readily be appreciated that there are some points of difference between the methods they suggest and those which should be adopted, for example, in preparing for publication in these Transactions; but the authors meet even this point very largely in their oft-repeated advice to study the Journal to which the proposed contribution is to be submitted, and to modify the style of the contribution in accordance therewith.

The authors give a list of abbreviations of the periodical publications most frequently cited. Their rules for abbreviation can be fully endorsed: although, by the way, the examples by no means follow the rules completely. It may be mentioned that in abbreviating for these Transactions their rule would be amended as follows: "The abbreviation should be as drastic as possible, with a view to economy of space, but it should never be carried to such an extent that ambiguity may arise." For instance, *physical* or its numerous foreign equivalents should never be abbreviated to *phys.* which may be taken for physical or physiological.

The book is a very useful addition to the library, the only comment being that it is unfortunate it could not have been priced at two or three shillings, when doubtless its circulation would have been very much wider; it is hoped, however, that it will meet with such success as to justify the publication of future and larger editions at a lower price.

The reviewer looks forward to the time when every author will accept the advice to read his typescript through some five or six times (including reading it aloud once or twice), shortening and embellishing it at each stage, before transmitting it for publication, and to the time when he will also read the proofs three or four times as advised!

**Collected Physical Papers of Sir J. C. Bose.** (Longmans, Green & Co.  
Pp. xiii + 404. Price 10s. net.)

We may quote from the foreword of Sir J. J. Thomson. "In addition to the purely physical papers, there are others which describe the beginnings of Sir Jagadis' application of physical methods to the study of living matter, a subject to which most of his work in recent years has been devoted. The papers make very agreeable reading for the author is never dull. Another aspect of these papers is that they mark the dawn of the revival in India of interest in researches in Physical Science; this, which has been so marked a feature of the last thirty years, is very largely due to the work and influence of Sir Jagadis Bose."

# ON THE EFFECT OF COLLOIDS IN THE ELECTRO- DEPOSITION OF SILVER FROM SILVER NITRATE SOLUTIONS.

By S. WERNICK, B.Sc.

(Received 21st February, 1928.)

It has long been known that the presence of small quantities of certain substances, generally of a colloidal nature, in electroplating solutions markedly affects the appearance of the deposit, the characteristic of the change being a smoother, generally whiter, deposit, brought about by a considerable reduction of the grain-size of the crystals. This grain-size reduction has at different times been ascribed to chemical reduction,<sup>1</sup> to the adsorption of the colloid by the cathode,<sup>2</sup> and lastly (and this possibly includes the last mentioned), to its action as a protective colloid.<sup>3</sup> Reducing capacity is, however, by no means common to all effective colloids, while Mathers and Leible<sup>4</sup> have shown that the relation between adsorption and efficiency as an addition agent is not a simple one. Mueller and Bahntje,<sup>5</sup> as a result of studying the effect of some five colloids in the electrodeposition of copper from  $\text{CuSO}_4$  solutions suggested a direct connection between the gold number of an added colloid and the grain-size of the deposit. A simple relation would be expected to hold from the fact that a gold number varies inversely with the degree of protection afforded by the colloid.

Freundlich and Fischer,<sup>6</sup> working with a fluosilicate and also a perchlorate solution, were unable to find a parallelism between the gold number and the effectiveness as an addition agent. They tried five colloids in the case of the fluosilicate bath and only three in the case of the perchlorate bath. Their reasoning appears open to two serious objections, however. The first is that they worked with a *lead* bath and compared this with a *gold* number; obviously, a fairer test would be to determine the addition agent effectiveness of various colloids in a gold plating bath, and for other metals to use in place of the gold sol the sol of the metal which was being deposited. The second objection is the purely subjective manner employed by them to test the value of their deposits; these results could only have been tentative. In the present investigation, silver nitrate solutions were employed. It is well known that the silver deposit obtained from these is extremely coarse and crystalline and, therefore, it makes a suitable starting-point for an attempt to measure the extent of the grain-size reduction achieved by addition of a given colloid.

<sup>1</sup> Betts, A. G., "Lead Refining by Electrolysis" (1908).

<sup>2</sup> Marc, R., *Z. physik. Chem.*, **67**, 410, 1909; **68**, 104, 1909; **73**, 685, 1910; **75**, 710, 1911; **81**, 641, 1913; Foerster, F., *Z. Elektrochem.*, **4**, 163, 1897; *ibid.*, **5**, 512, 1899; Senn, H., *ibid.*, **11**, 229, 1905; Kohlschuetter, V., and Schacht, H., *ibid.*, **19**, 172, 1913; Grube, G., and Reuss, V., *ibid.*, **27**, 45, 1921.

<sup>3</sup> Mueller, E., and Bahntje, P., *Z. Elektrochem.*, **12**, 317, 1906.

<sup>4</sup> Mathers, F. C., and Leible, A. B., *Trans. Amer. Electrochem. Soc.*, **31**, 271, 1917.

<sup>5</sup> Freundlich, H., and Fischer, J., *Z. Elektrochem.*, **14**, 49, 1908.

It is suggested that it is the state of aggregation of the silver during the process of deposition which exercises a fundamental, if not the most important, effect in determining the grain-size; this aggregation during deposition is considered to be not dissimilar to that obtaining in a colloidal silver solution. It was therefore considered that a determination of the protection afforded by certain colloids in preventing the precipitation of the colloidal particles present in a silver sol compared directly with the reduction in grain-size which these same colloids effected in a silver nitrate solution might throw considerable light on the validity of the "protective colloid" theory. It will be seen that the first portion of the investigation is in effect a "gold number" determination using a silver instead of a gold sol. The figures obtained may on analogy be termed "silver numbers," and are defined as the number of milligrams of a given colloid which is just sufficient to prevent the precipitation of 10 c.c. of a standard silver sol on addition of 1 c.c. of a standard electrolyte. The determination of the beneficial effect of the colloid has in all previous researches been treated qualitatively. Although it is possible to obtain a certain amount of useful information by intelligent inspection of the deposit, it was thought desirable to adopt some means of giving a quantitative value to the quality of the deposit. Microphotographs were obtained and the number of granules present in a given area counted, in this investigation.

#### Determination of Silver Numbers.

As has been experienced in the determination of gold numbers several factors operate to render the allocation of a single definite number to represent a given colloid extremely difficult if not impossible. Not only does the same colloid obtained from different sources give widely varying results, but the latter are found to vary with the age of the protective colloid, the mode of preparation of the silver sol, the nature of the salt used to effect precipitation and the varying manner in which this precipitation manifests itself. An initial difficulty was the preparation of a stable silver sol of sufficient concentration to show a distinct colour change when the precipitation point was reached. If possible, it was considered desirable to keep the sol clear of foreign organic substances which might have a protective effect on the one hand, and inorganic salts which might have a precipitating effect on the other. Attempts to utilise the pure sols obtained by Kohlschuetter's<sup>6</sup> method and also Bredig's<sup>7</sup> method were, however, unsuccessful owing to their comparative instability, and the silver sol used was eventually that obtainable by Carey Lea's method. Silver nitrate was the precipitating salt used, since this is the electrolyte encountered by colloid aggregates in the silver nitrate solution. The colour change found to occur with silver sols was neither as sharp nor as distinct as obtains in gold number determinations, while it does not appear to occur at all in some colloids. With one or two colloids, a series of states of aggregation of the colloid particles is indicated before final precipitation, the sols showing a gradation of colour, then a change from translucency to opaqueness and finally precipitation. Since only this final precipitation is common with all the colloids which were employed, it was considered best to take the "end-point" in each case as being reached at the first sign of incipient settling of the silver particles.

In regard to the precipitating agent it was found that silver nitrate

<sup>6</sup> Kohlschuetter, V., Z. Elektrochem., 14, 49, 1908.

<sup>7</sup> Bredig, Anorganische Fermente: Leipzig, 1901.

could not be used in every case: *e.g.*, in the case of sodium oleate, a precipitate forms, while in several other cases, *e.g.*, egg albumin, casein, peptone, the silver nitrate was found to precipitate the protective colloid added. With these colloids, it was therefore necessary to use another electrolyte, and KCl was found to be a satisfactory substitute.  $\text{KNO}_3$  was also found suitable as a precipitant, though slower in its action. The "end-point" of all three precipitants was found to be approximately the same. The calculated silver numbers and their reciprocals, which are proportional to the protection which the colloid affords the silver sol, are given in the following table:—

No.	Protective Colloid.	Silver Number.	Recip. Silver Number.
1	Gum tragacanth . . .	1.18	0.85
2	Gum acacia . . .	4.64	0.22
3	Gum arabic . . .	5.92	0.17
4	Gelatin . . .	7.86	0.13
5	Starch . . .	9.22	0.11
6	Sodium oleate . . .	231.8	0.004
7	Casein . . .	0.67	1.49
8	Peptone . . .	6.77	0.15
9	Isinglass . . .	5.52	0.19
10	Dextrin . . .	28.36	0.035
11	$\beta$ -naphthol . . .	$\infty$	0.00
12	Glucose . . .	440.6	0.002
13	Dextrose . . .	$\infty$	0.00

### Preparation of Deposits.

The apparatus used in obtaining deposits was an adaptation of Sand's electrolytic stand. The electrolyte was placed in a small beaker, the anode consisting of a small cylinder of silver gauze, completely surrounding the cathode, which consisted of a platinum strip, attached to a specially designed holder, which had previously been well coated with silver. The latter was soldered to a copper rod enclosed within a tightly fitting rubber tube, itself enclosed in a glass tube so as to provide the minimum of friction on rotation.

The holder of the platinum cathode was shaped as in Fig. 1 having three prongs, the central one shorter and pointed, the point being slightly bent away from the plane of the holder, so that the cathode could be easily slipped between the latter and those at either end, while the point entered a small hole made in the cathode. This holder was found to provide a satisfactory contact having the advantage of easy and rapid attachment and removal of the cathode. It was rotated at a speed of about 300 revs. per minute. The connection with the moving cathode was maintained by means of a mercury contact. A diagrammatic representation of the anode and cathode is shown in Fig. 2.

The platinum cathode measured  $1.5 \times 1.0$  cm. and was previously cleaned by washing in nitric acid, immersing for a short time in hot soda solution and then scouring with fine pumice. The anode, which became discoloured after electrolysis, was cleaned in nitric acid and thoroughly washed before use. The current employed was adjusted at the beginning of each run to 20 millamps., this being found a convenient strength after some trial. It

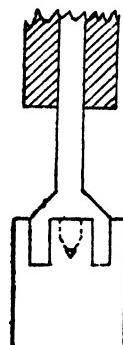


FIG. 1.

was generally maintained closely throughout the run without further adjustment. The current density was thus 1·33 amps./dm.<sup>2</sup> (12·36 amps./ft.<sup>2</sup>).

Sufficient colloid was added in each case to produce a content of 0·01 g. in 50 c.c. of the solution (*i.e.*, 0·02 per cent.). The time for each run was in most cases one hour, although in one or two cases where the structure

did not appear to be sufficiently developed, the time was prolonged beyond this period. Where the crystals were very large, *e.g.*, as when a solution containing only neutral silver nitrate or where a comparatively useless addition agent like glucose was added, the outgrowth, particularly at points of high current density, were so large that the motion of the electrolyte was sufficient to remove the later crystal growth. Since however the more even growth on the surface would have been curtailed by shortening the time of the run, each run was nevertheless continued for a minimum period of one hour. The temperature of the electrolyte was approximately 16° C. At the end of each run, the cathode was removed, washed successively in water, alcohol, and ether, and dried in a current of warm air.

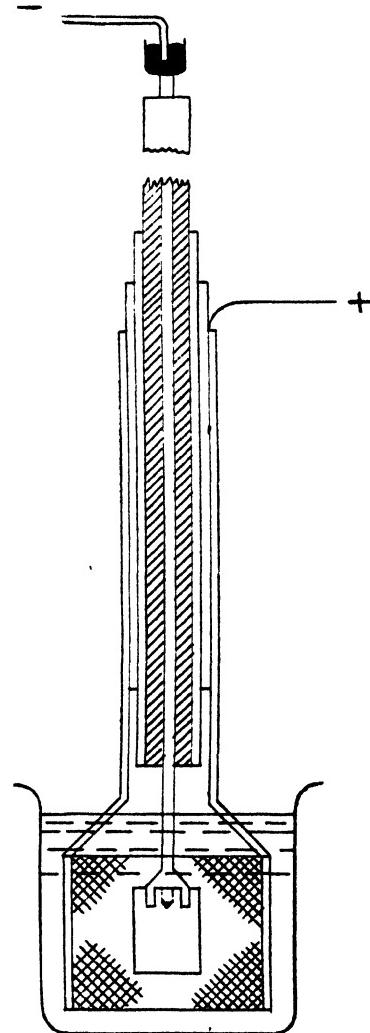


FIG. 2.

#### Estimation of the Fineness of the Deposit.

The original intention was to examine the structure of a section of the deposit cut near the centre of the cathode, but it was found impossible to handle some of the deposits owing to the looseness and large size of the crystals. Even in the case of the finer crystal structures which were comparatively more adherent, although these could be safely embedded in a suitable matrix, cutting of the section even with a fine wheel dislodged the deposit. In no case was a deposit obtained the adherence of which could be at all compared with that encountered in the deposition of the commoner metals, *e.g.* nickel or copper—or silver as deposited from the double cyanide solution.

The only alternative was to obtain microphotographs of the macroscopic aspect of the deposit, although for the same reason it was out of the question to grind the surface flat, and etching was therefore useless. Nevertheless, examination of the crystals through the microscope at various depths of the deposit showed no appreciable change in the appearance of the deposit. It appeared on the whole to indicate that the number of crystals

viewed at a given level varied very little from those at any other depth in the immediate neighbourhood of the surface.

The cathode was accordingly mounted on a glass slide and illuminated with a "pointolite" lamp, and photographs were taken using 70 H & D negatives at exposures of 6 to 8 minutes. The magnification employed was 100 diameters in each case with the exception of deposits obtained using  $\beta$ -Naphthol and Dextrose as addition agents, these being so coarse that a lower magnification—45 diameters—was employed.

The number of crystals per sq. cm. of surface at several positions on the microphotograph showing various degrees of fineness was counted and these figures averaged, the results being as under :—

Electrolyte.	Appearance of Deposit.	Average No. of Crystals per cm. <sup>2</sup> .
AgNO <sub>3</sub> alone . . . . .	Coarsely crystalline; big variation in sizes of crystals	71 × 10 <sup>4</sup>
AgNO <sub>3</sub> + 0·02 per cent. gum tragacanth . . . . .	Close-grained deposit . . . . .	523 × 10 <sup>4</sup>
" " gum acacia . . . . .	Very small crystals . . . . .	356 × 10 <sup>4</sup>
" " gum arabic . . . . .	Close-grained deposit; white . . . . .	380 × 10 <sup>4</sup>
" " gelatin . . . . .	Small crystals; white deposit . . . . .	335 × 10 <sup>4</sup>
" " starch . . . . .	Bright deposit; varying crystal size . . . . .	218 × 10 <sup>4</sup>
" " dextrin . . . . .	Dark deposit; close-grained . . . . .	554 × 10 <sup>4</sup>
" " glucose . . . . .	Large flat crystals; white . . . . .	97 × 10 <sup>4</sup>
" " $\beta$ -naphthol . . . . .	Voluminous, non-adherent crystals . . . . .	28 × 10 <sup>4</sup>
" " dextrose . . . . .	" " "	31 × 10 <sup>4</sup>

It is seen that, with the exception of dextrin, there appears to be a rough relationship between the reciprocal silver number and the number of crystals per sq. cm. The apparently anomalous behaviour of dextrin, which is much more effective in reducing the grain-size than would be expected from its silver number remains unexplained. Unlike some other colloids, it appears actually to improve in its protective capacity on standing, and this is suggestive. Although there is no *direct* relationship between the two properties, a marked increase in the silver number, as, for example, in the case of  $\beta$ -naphthol and dextrose, which have no protective action at all on the silver colloid, is well reflected in a corresponding inability to reduce the crystal size of the deposit. The very low number of crystals per unit area in these cases (actually lower than in the case of the pure silver nitrate electrolyte) is due to the very large growth of these crystals; in the case of the AgNO<sub>3</sub> electrolyte alone *small* as well as large crystals were formed, and therefore brought up the average figure.

The absence of a simple relationship is ascribed to two causes; first, the difficulty experienced in determining the silver number as accurately, for example, as it is possible to determine the gold number; secondly, the operation of other factors affecting the ultimate crystal size. Nevertheless, the fact that some relationship is apparent indicates that the mechanism of the cathode reactions in electrodeposition may be rationally and substantially accounted for in a modification of the "protective colloid" theory. Although it would appear that there are other controlling influences, it would seem that this protective action of the colloid manifests itself sufficiently in the majority of cases to enable it to be detected by some determination analogous to that of the gold number, represented in this research by the "silver number." Although it might be difficult and even impossible to arrive at a comparison between two colloids the effects of which were not

far removed from one another, nevertheless, it would be possible to differentiate between a colloid likely to have a beneficial effect on the deposit, and one which would have no such effect, or possibly an adverse effect.

Whether this effect would be useful in seeking for "beneficial" colloids for other solutions depends in large measure on the properties of the metal sol which would have to be prepared in each case, *e.g.*, a copper sol in the case of copper solutions, etc. Since these solutions are generally used under distinctly acid conditions, this would impose a further variable which would have to be taken into account, since one or two experiments in the case of the silver nitrate solution indicated that the  $\rho_H$  of the solution distinctly affected the efficiency of the colloid.<sup>8</sup> Presumably the more stable the metal sol, the better the conditions for testing the colloid theory, and it would thus appear that the deposition of gold offers the best field for experiment on this head, since the gold sol is so remarkably stable. (Early experiment in this research showed that a gold sol could be kept without special precautions for some two years without any sign of marked deterioration.) It is hoped that such a research will be carried out and a comparison with the standard gold number figures made.

### Summary.

1. The "silver numbers" of a number of colloids commonly used to reduce grain-size were determined.
2. Silver sols, prepared by the methods of Kohlschuetter and Bredig, which are free from electrolytes were first tried in this determination, but were found to be not sufficiently concentrated and too unstable; Carey Lea's sol was therefore used.
3. Various modes of determining the silver number were tried, the precipitation method of Zsigmondy being found best. Silver nitrate cannot be used as a precipitant for all colloids, but other precipitants were found to have approximately the same effect. A minimum strength of precipitant is however necessary to effect precipitation.
4. Silver deposits were obtained from a neutral silver nitrate solution containing the different colloid whose silver number had been determined, and microphotographs of these deposits were taken. The number of crystals per unit area was determined, this being taken as a measure of the fineness of the deposit.
5. With the exception of dextrin, it was found that there was a relationship between the silver number and the fineness of the deposit. Controlling factors other than the protective effect however also enter, but the latter effect is a strong one.
6. The relationship is not sufficiently direct to enable a comparison between two colloids having approximately similar effects to be made; but it is quite sufficiently marked to enable "good" colloids to be differentiated from "bad."

In conclusion, the author wishes to express his thanks to Dr. H. Sand for his interest and valuable advice throughout the course of this investigation.

<sup>8</sup> See "The Rôle of Colloids in Electrolytic Metal Deposition," H. J. S. Sand, 4th Report on Colloid Chemistry, 1922, p. 349, for other suggested factors affecting the efficiency of the colloid.

# OVERPOTENTIAL AT METALLIC CATHODES. CADMIUM AND ANTIMONY IN NEUTRAL AND ALKALINE SOLUTIONS.

By JULIUS GRANT, M.Sc.

(Received 2nd February, 1928.)

The experiments described for silver cathodes<sup>1</sup> have been extended to cadmium. In general, the same experimental procedure was observed, and the results are summarised below. A few results for antimony not previously published, are included for comparison.

## Cadmium.

The cadmium cathode was a solid cylinder 0·6 cm. in diameter, and having an area of 3 sq. cm. The anode was platinum.

As in the case of silver, difficulties in obtaining reproducible results were experienced when the precautions outlined in the previous paper were not taken. These difficulties were associated with the formation in the electrolyte of a dirty-white precipitate which appeared to be cadmium hydroxide, and by evidence of cathodic disintegration which resulted in the transport of cadmium (possibly in the colloidal state) from the cathode to the anode, even when the former was surrounded by a porous pot.

The variations of overvoltage with time, current density (using the direct and commutator methods) and the duration of the interval of the commutator (decay of polarisation), were in each case of the same nature as those obtained for silver. The principal results are summarised in Table I. in which the  $\rho_H$  voltages, the direct, commutator, and decay curve overvoltages, respectively, the critical current densities, and the times required to obtain constant readings by the commutator method are shown.

In the graph shown in Fig. 1 the abscissæ represent the  $\rho_H$  voltages, and the ordinates the corresponding overvoltages as obtained by the three methods. The numbers attached are for the purposes of identification with the results shown in Table I. The straight line shown for comparison corresponds with the relationship  $2\rho_H + w = 2\cdot75$ .

<sup>1</sup> J. Grant, *Trans. Faraday Soc.*, **24**, 225, 1928.

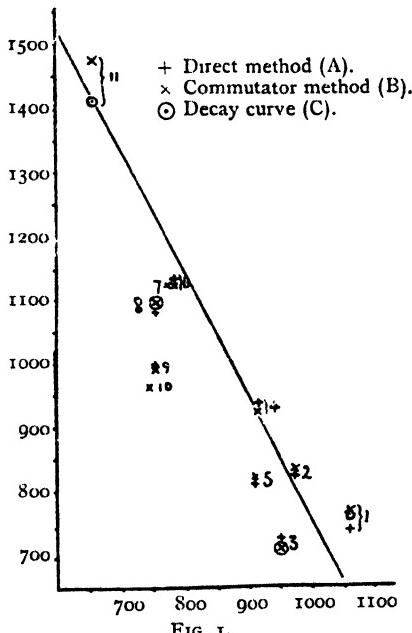


FIG. 1.

TABLE I.

No.	Solution.	$\rho_H$ Voltage (m.v.).	Overvoltages.			Critical C.D.	Time (Mins.).
			Direct.	Comm.	Decay Curve.		
1	N NaOH . . .	1060	735	765	760	25	35
2	Ca(OH) <sub>2</sub> (semi-sat.)	975	825	830	—	7	3
3	Ba(OH) <sub>2</sub> (semi-sat.)	955	720	707	705	10	20
4	N/37 N Et <sub>3</sub> OH . . .	920	930	920	—	5	10
5	N/46 N Me <sub>2</sub> OH . . .	915	810	815	—	10	7
6	Borax (semi-sat.) . . .	785	1130	1125	—	50	10
7	HNa <sub>2</sub> PO <sub>4</sub> (sat.) . . .	780	—	1125	—	—	25
8	HNa <sub>2</sub> PO <sub>4</sub> (semi-sat.) . . .	760	1080	1095	1095	25	12
9	N Am <sub>2</sub> CO <sub>3</sub> . . .	760	990	990	—	10	10
10	N NaHCO <sub>3</sub> . . .	750	—	960	—	150	3
11	N Na <sub>2</sub> SO <sub>4</sub> . . .	655	—	1475	1415	30	20

In Figs. 2 and 3 the curves are shown from which the three values of

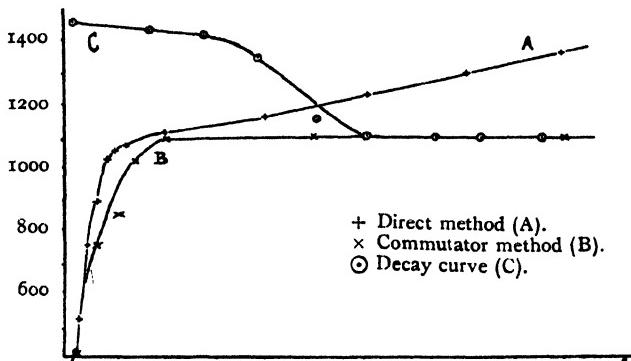


FIG. 2.

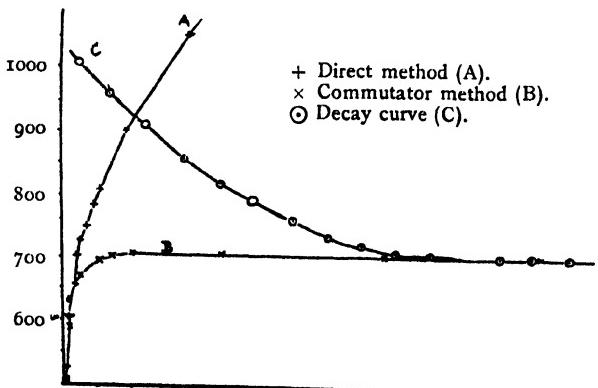


FIG. 3.

the overvoltage were obtained in the cases of the electrolytes semi-saturated disodium hydrogen phosphate and semi-saturated barium hydroxide, respectively (cf. Figs. 2 and 3 on pages 229 and 230).

## Antimony.

Some of the results obtained have already been referred to elsewhere,<sup>2</sup> and it is proposed to deal only with those hitherto unpublished. These are summarised in Table II., which is analogous to Table I., and are of the same nature as those obtained for silver and cadmium.

TABLE II.

No.	Solution.	$\rho_H$ Voltage (m.v.).	Ovoltages.			Critical C.D.	Time (Min.).
			Direct.	Comm.	Decay Curve.		
1	8 <i>N</i> NaOH . .	1100	—	640	—	17	20
2	<i>N</i> NaOH . .	1060	700	715	690	15	30
3	<i>N</i> /10 NaOH . .	990	—	730	—	15	15
4	<i>N</i> NH <sub>4</sub> OH . .	980	—	500	—	4	—
5	Ca(OH) <sub>2</sub> (semi-sat.)	975	460	470	460	100	15
6	Ba(OH) <sub>2</sub> (semi-sat.)	955	650	635	475	10	35
7	<i>N</i> Na <sub>2</sub> CO <sub>3</sub> . .	940	—	740	—	15	7
8	<i>N</i> /37 NEt <sub>4</sub> OH . .	920	860	860	865	6	7
9	<i>N</i> /90 NMe <sub>4</sub> OH . .	895	—	935	—	3	7
10	HNa <sub>2</sub> PO <sub>4</sub> (semi-sat.)	760	1200	1220	1220	40	15
11	<i>N</i> Am <sub>2</sub> CO <sub>3</sub> . .	760	—	790	—	40	8
12	<i>N</i> /10 NaHCO <sub>3</sub> . .	750	—	960	—	40	20
13	<i>N</i> Na <sub>2</sub> SO <sub>4</sub> . .	655	1270	1240	1245	80	20

In Fig. 4 the overvoltages are again plotted against  $\rho_H$  voltages, and a straight line represented by the equation  $2\rho_H + w = 270$  has been drawn for comparison.

## Conclusions.

(1) The main conclusions drawn from the above results are in agreement with those obtained in the case of silver.<sup>1</sup>

(2) Where the overvoltages have been plotted as a function of the  $\rho_H$  voltages it is seen that many of them fall on or near the straight line  $2\rho_H + w = \text{constant}$ , though as in the case of silver, there are exceptions which are neither explainable by experimental error nor by the poor buffering capacities of the solutions concerned. It may be noted, however, that solutions of ammoniacal salts and of bicarbonates are principally concerned. Since such solutions tend very readily to give off a gaseous

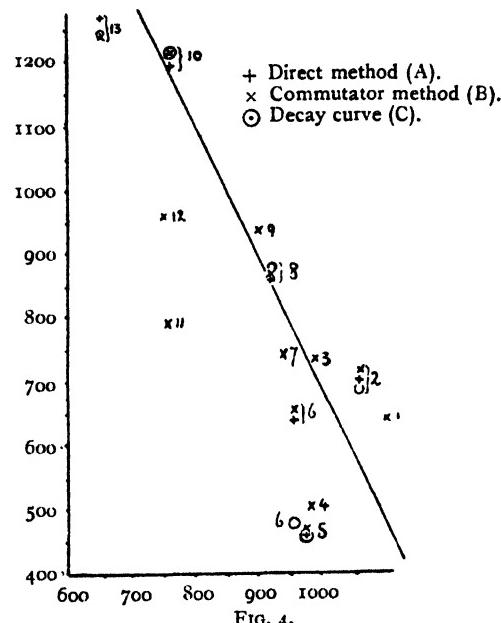


FIG. 4.

constituent (especially at the increased temperatures probably produced locally in the neighbourhood of the cathode), it is probable that the resistance to the evolution of electrolytic hydrogen is lowered. The effect of this would be expected to manifest itself particularly when high overvoltages are concerned, as with cadmium and antimony, but less for the lower overvoltages of silver.

It may be urged that the neutral solutions should not be included in a study of the dependence of overvoltage on  $\rho_H$  value, since it is impossible to determine the latter accurately in the electrode layer during electrolysis owing to the lack of buffering power. Further, the overvoltage results of the decay curves are largely dependent on the polarisation capacity of the electrodes, and the same reliance can therefore not be placed on them as on those obtained by the other methods. If we exclude values obtained in neutral solution and also those in which the decay curve results differ very greatly from those obtained by the other methods, the most serious deviations from the straight lines are removed. This holds particularly also for the silver results; with regard to these it may also be pointed out that deviations from the straight line are somewhat magnified by the fact that overvoltages have been plotted on twice as large a scale as  $\rho_H$  voltages in order to give the straight line the same slope in all cases.

In conclusion, the author wishes to express his indebtedness to Dr. H. J. S. Sand, F.I.C., at whose suggestion and under whose supervision the above experiments were carried out.

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## THE ELECTRO-DEPOSITION OF IRON-NICKEL ALLOYS.

BY S. GLASSTONE AND T. E. SYMES.

*Received 3rd April, 1928.*

### PART II.

In a previous communication<sup>1</sup> an account was given of an investigation of the composition of iron-nickel alloys deposited electrolytically from mixed sulphate solutions buffered by means of sodium acetate and acetic acid at 15°. The present paper contains the results of some experiments which were made with the object of determining whether the presence of certain anions or cations had any influence on the composition of the deposited alloy. In the first place a mixed sulphate solution was buffered at  $\rho_H$  5·2 by means of boric acid instead of the acetic mixture; in another experiment the electrolyte contained 0·5 g.-equiv. of sodium chloride per litre in addition to the sulphates and the acetate buffer, whilst in the third case the iron and nickel salts used were partly in the form of the double ammonium sulphates. All the work was carried out at a temperature of roughly 15°.

<sup>1</sup> Part I., *Trans. Faraday Soc.*, 1927, 23, 213.

### Experimental.

*General.*—The arrangement of apparatus, cathodes, anodes, analytical method and general experimental details were all the same as described in the previous communication.<sup>1</sup>

#### Preparation of Electrolytes.

A. *Solution buffered by boric acid.*—A solution containing 1 g.-equiv. per litre of both nickel and ferrous sulphates was made up and excess of solid boric acid added; this electrolyte had a  $p_H$  of 5.2 to 5.3 and did not vary appreciably during electrolysis.

B. *Solution containing chloride ions.*—The electrolyte contained 0.2 g.-equiv. of ferrous sulphate, 1.8 g.-equiv. of nickel sulphate, and 0.5 g.-equiv. of sodium chloride in 1 litre, together with the sodium acetate and acetic acid required for a solution of  $p_H$  5.2.

C. *Solution containing ammonium ions.*—The electrolyte was made up from 0.02 g.-equiv. each of ferrous and ferrous ammonium sulphates and 0.18 g.-equiv. each of nickel and nickel ammonium sulphates in 1 litre, together with the sodium acetate and acetic acid required for a solution of  $p_H$  4.0.

### Results.

The curves in Fig. 1 show the variation in composition of the alloys deposited at different C.D.'s from the three solutions A, B and C described above; the corresponding curves for the sulphate-acetate solutions used previously are XVIII., XVI. and XI. respectively.<sup>1</sup> If we compare curves A and XVIII. it will be seen that they are almost identical; the maximum iron content of the alloy in the former case is about 86 per cent. and in the latter 87.6 per cent. It is probable, therefore, that neither borate nor acetate ions, their concentration in the two cases being greatly different, have any appreciable influence on the composition of the deposited alloy.

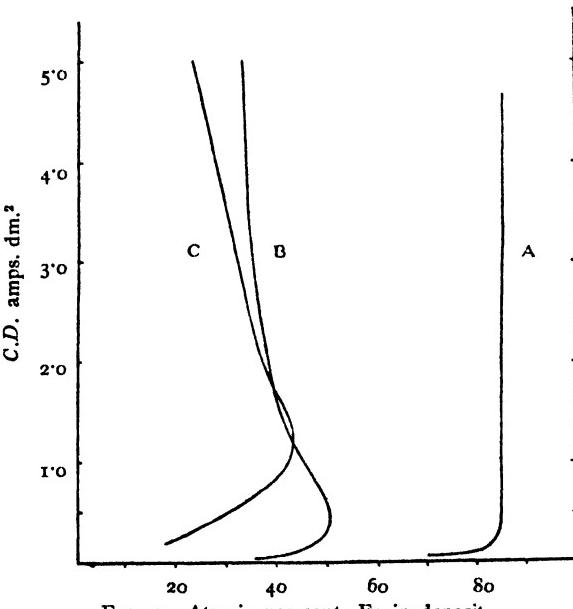


FIG. 1.—Atomic per cent. Fe in deposit.  
(Temperature 15°).

A comparison of curves B and XVI. shows that the general behaviour is very similar; in the former case the maximum iron content of the alloy is slightly greater than in the latter—51 per cent. against 48.9—but this

may be connected with slight changes in the rate at which the iron and nickel ions diffuse up to the cathode.

Curve C is almost identical in shape with curve XI. although its position is somewhat different; the former appears to have been moved along the *C.D.* axis but the maximum iron content of the alloy is almost the same in both cases—about 42·5 per cent. A comparison of the curves gives the impression that in the former case alloy deposition occurs less readily so that a higher *C.D.* is required before the rate of discharge of ferrous ions is equal to the rate of their diffusion to the cathode; that is, the maximum iron content is reached at a higher *C.D.* with solution C than with solution XI. In agreement with this view it has been found that the current efficiency for alloy deposition is less in the presence of ammonium ions.

*Conclusion.*—Within the limits of the present experiments it appears that anions and cations do not have any appreciable influence on the relative tendency of iron and nickel to deposit from solutions containing *simple* ions of both metals. They may, however, have some effect on the diffusibility of the ions and the current efficiency; slight changes have been observed in the appearance of the deposited alloys with changes in the nature of the electrolyte.

### PART III.

All the previous experiments on the electrodeposition of iron-nickel alloys carried out by the present authors have been made at 15°;<sup>1</sup> a

number of observations on the variation of the composition of the alloys with changing *C.D.* have now been made for a series of electrolytes at temperatures of 53° and 90°. The results of these experiments are described below.

#### Experimental.

The experimental details were identical with those already described in Part I. of this series.<sup>1</sup> A gas heated thermostat was used for the experiments at 53°

and a hot-water bath for those at 90°.

*Experiments at 53°.*—The solutions used were I., III., IV., V., VI., VII., VIII., IX., X., XIV., XVI., XVIII., and XX. of the previous work. The

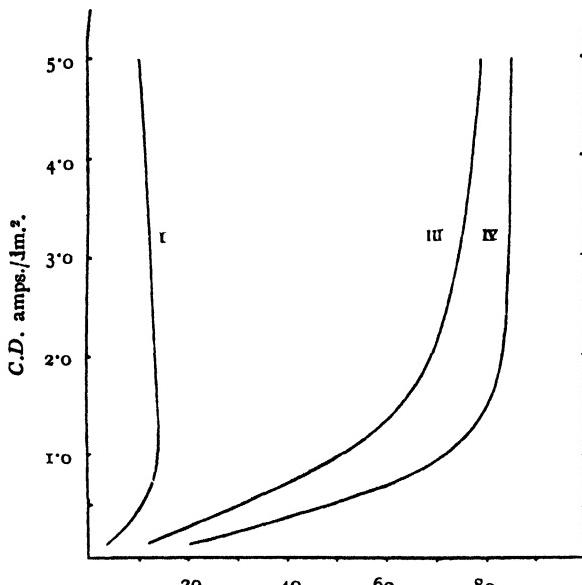


FIG. 1.—Atomic per cent. Fe in deposit. (Temperature 53°.)

<sup>1</sup> *Trans. Faraday Soc.*, 1927, 23, 213.

hydrogen ion concentrations were determined at ordinary temperatures; the actual values are not very important, although in this case, owing to the fact that the dissociation constant of acetic acid does not vary appreciably between  $15^{\circ}$  and  $60^{\circ}$ , they will be very little different from those at  $15^{\circ}$ .

*Results.*—The variation in composition of the alloys with C.D. are given in Figs. 1, 2, 3 and 4; the curves should be compared with those bearing the same Roman numerals in Figs. 1, 2, 3 and 4 of Part I. of this series (pp. 218, 219). The curve marked "Xs" was drawn from results obtained when the solution X was stirred, the cathode being rotated approximately 500 times per minute.

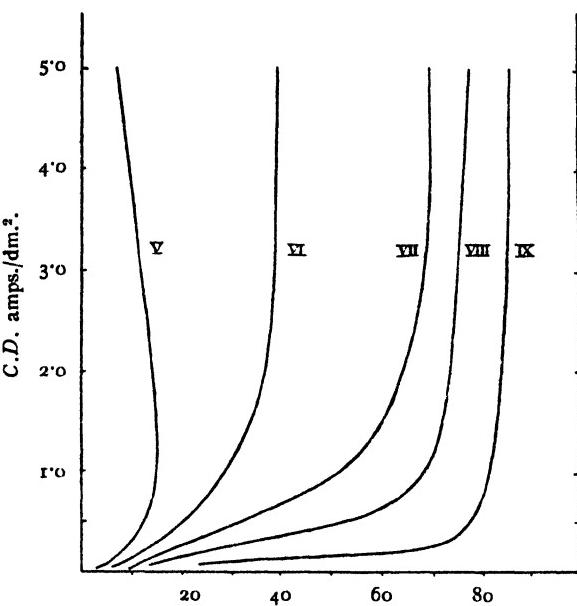


FIG. 2.—Atomic per cent. Fe in deposit. (Temperature  $53^{\circ}$ .)

The mean current efficiencies for alloy deposition at different C.D.'s with solutions of varying  $p_H$  are given in Table I.

The mean current efficiencies are appreciably greater than those at ordinary temperatures. This is due to the fact that the initial deposition potentials of the iron-nickel alloys are lowered in amounts varying from 0.14 to 0.20 volt. as the temperature is in-

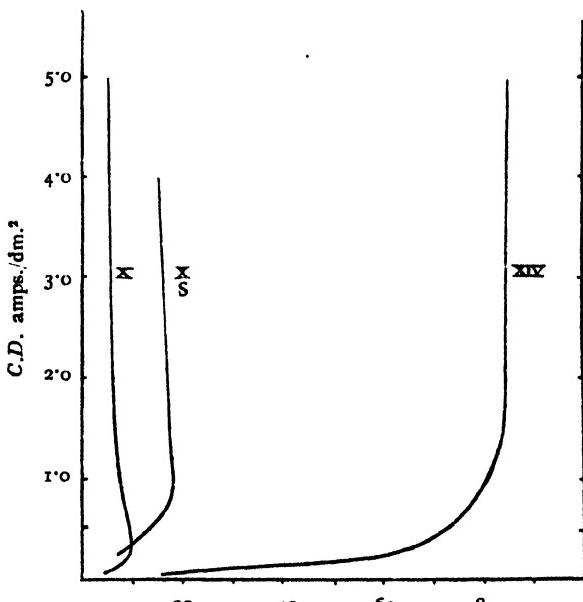
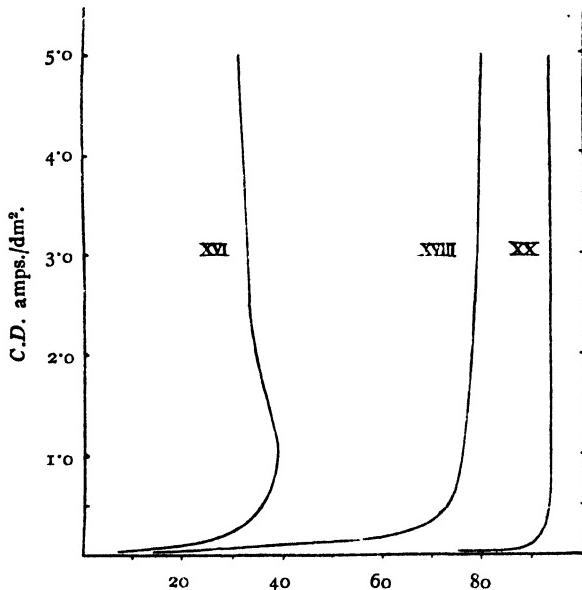


FIG. 3.—Atomic per cent. Fe in deposit. (Temperature  $53^{\circ}$ .)

TABLE I.

C.D. amps./dm. <sup>2</sup>	Per Cent. Current Efficiency for Alloy Deposition.		
	$\rho_H 3^{\circ}2$	$\rho_H 4^{\circ}0$	
		$\rho_H 5^{\circ}2$	$\rho_H 5^{\circ}2$
0·1	8	17	67
0·25	9	24	70
0·5	10	32	85
1·0	15	49	90
2·0	34	64	90
4·0	55	65	90

increased from  $15^{\circ}$  to  $53^{\circ}$ <sup>2</sup> whereas the hydrogen overvoltage is at the same time only reduced by about 0·08 volt (unpublished measurements).

FIG. 4.—Atomic per cent. Fe in deposit. (Temperature  $53^{\circ}$ .)

iron deposited from various solutions. The results obtained at  $53^{\circ}$  have been collected together in Table II.

TABLE II.

Fe/Fe + Ni Per Cent. in Solution.	Minimum Per Cent. Iron in Alloy.					Maximum Per Cent. Iron in Alloy.				
	2.	10.	30.	50.	70.	2.	10.	30.	50.	70.
$\rho_H 3^{\circ}2$	3·9	—	—	12·0	22·7	14·4	—	—	79·5	86?
" 4°0	3·2	5·3	10·7	14·6	23·6	15·3	39·0	70·0	79?	86·5
" 5°2	—	7·1	—	14·1	—	—	38·5	—	80·0	—

These values confirm the conclusion, drawn from observations at ordinary temperatures, that the hydrogen-ion concentration of the solu-

<sup>2</sup> Glasstone, *J. Chem. Soc.*, 1926, 129, 2897.

tion has no influence on the relative tendencies of iron and nickel to be deposited electrolytically from a solution containing both metals. One of us<sup>2</sup> has observed that the electrodeposition potential of an iron-nickel alloy approaches more closely that at which pure nickel is deposited the higher the temperature; on the basis of this fact and the theory already outlined<sup>3</sup> it was stated that: "At higher temperature . . . we should expect the deposits from a given solution to contain much less iron than at ordinary temperatures and the increase of the proportion of iron with increasing C.D. to be much more gradual. When the amount of iron in the electrolyte is increased the behaviour should approach more closely that found at ordinary temperatures." The results obtained in the present work are in complete agreement with this prediction. With those solutions which contain a relatively small amount of iron (*e.g.*, VI., VII. and XVI.) it can be clearly seen that the rate of increase of iron content with increasing C.D. is much less at 53° than at 15°; when the solution contains a large proportion of iron, however (*e.g.*, VIII., IX., XIV., XVIII. and XX.), there is very little difference between the shapes of the curves obtained at the two temperatures. Further, a comparison of the sets of curves for 15° and for 53° shows that the alloys deposited under similar conditions contain less iron at the higher temperature; this conclusion is also reached by comparing the minimum and maximum iron content of the alloys deposited from the same solutions at the two temperatures. The mean results are given in Table III.

TABLE III.

Per Cent. Iron in Deposit from Solutions Containing					
	2 Per Cent. Fe.	10 Per Cent. Fe.	30 Per Cent. Fe.	50 Per Cent. Fe.	70 Per Cent. Fe.
Minimum 15°	4·4	11	21	22	36
" 53°	3·5	6·2	11	13	23
Maximum 15°	22·6	47·9	77·5	87·3	93·5
" 53°	14·9	38·8	70·0	79·5	86·5

An examination of the results for the minimum iron content of the alloys obtained at 53° shows that even when the solution contains somewhat less than 10 per cent. of the total metal as iron the initial deposit at very low C.D.'s contains relatively less iron than does the electrolyte; at 15°, however, this only occurs when the solution contains at least 20 per cent. of the total metal as iron. This is in agreement with the view expressed in previous papers (*loc. cit.*) that iron retards the change from metastable to stable nickel to a smaller extent at increased temperatures and so the latter metal is more readily deposited.

The alloys with the maximum proportion of iron always contain relatively more of this metal than does the electrolyte, but the maxima are less than those at ordinary temperatures. After the maximum is reached the C.D.-composition curves show that the subsequent decrease of the iron content of the deposit with increasing C.D. is not so marked or so frequent as at 15° in spite of the increased current efficiency (compare curves I., VI.

<sup>2</sup> *J. Chem. Soc.*, 1926, 129, 2887.

and XVI. for the two temperatures); this is undoubtedly due to the increased rate of diffusion at the higher temperature. In more dilute solutions, particularly those containing a small proportion of iron, the depletion of the iron concentration in the vicinity of the cathode is quite appreciable; this may be seen by comparing the curve for solution V. (maximum 15·3 per cent. iron) with that for the dilute solution X. (maximum 10·5 per cent. iron). As before, the result of stirring the electrolyte (Xs, Fig. 3) is to increase the maximum proportion of iron in the alloy—from 10·5 per cent. to 18·0 per cent. in the particular case under discussion. When the iron content of the solution is high the effect of dilution is not appreciable; a comparison of curves IX. and XIV. shows that the maxima are almost identical. The influence of diffusion is thus similar to that observed at ordinary temperatures although not so marked.

*Experiments at 90°.*—The variation in the composition of the alloy with C.D. for solutions I. and III. ( $\rho_H$  3·4) and V. and VIII. ( $\rho_H$  4·2) is shown in Fig. 5; as far as can be seen from these curves the relative tendencies for iron and nickel to deposit is again independent of the hydrogen-ion concentration of the electrolyte. The actual values of  $\rho_H$  at 90° have been calculated to be about 0·2 units greater than at ordinary temperatures; this alteration is immaterial

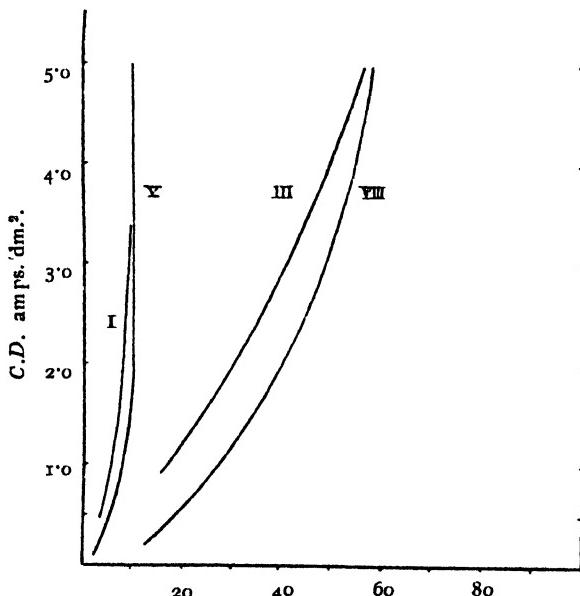


FIG. 5.—Atomic per cent. Fe in deposit. (Temperature 90°.)

as long as the actual  $\rho_H$  remains constant during each set of experiments. The current efficiencies, as expected, were found to be greater than at 53°, especially with the solutions containing a small proportion of iron.

In the case of the solution of  $\rho_H$  4·2 containing 2 per cent. of the total metal as iron the deposit at very low C.D.'s was found to contain 1·2 per cent. of iron; hence even when the solution contains a very large excess of nickel it is possible for the initial deposit at high temperatures to contain relatively more nickel than does the solution. This indicates that the retarding effect of iron on the deposition of stable nickel has been greatly diminished (see p. 375 above). As the C.D. is increased it is seen from the curves in Fig. 5 that the amount of iron in the deposit increases gradually; this rate of increase is much less than at 53°. At a temperature of 90° iron can be deposited reversibly whilst there is only a small over-voltage (about 0·07 volt) for nickel deposition; the deposits from a solution containing these two metals will thus vary with C.D. in the same way as

those from an electrolyte containing two metals capable of forming solid solutions, e.g., copper and cadmium, which can be deposited almost reversibly. In such cases it has been found<sup>4</sup> that as the *C.D.* is increased the deposit contains increasing amounts of the less noble metal, and at very high *C.D.*'s it may actually contain relatively more of this metal than does the electrolyte. This result is generally ascribed to the protective effect which the more noble metal has on the baser component of the alloy; the latter thus becomes more readily deposited. This behaviour is in agreement with the results obtained for nickel-iron alloys at 90°; owing to the fact that the deposition potentials of the two metals are fairly close together (iron - 0.46 and nickel - 0.31) the rate of increase of the proportion of the less noble metal—iron—with increasing *C.D.* is probably greater than it is with the copper-cadmium alloys. Iron may still have a slight retarding effect on the deposition of nickel, but the shape of the curves in Fig. 5 shows that this must be very considerably less than at ordinary temperatures. The tendency for the proportion of iron in the deposit to increase with increasing *C.D.* will be opposed by the decreased protective effect of the more noble metal (nickel) and its decreased deposition potential as the alloy contains relatively less of this constituent and so a point of balance, at which the deposit contains a maximum amount of iron will be reached at a high *C.D.* The curves in Fig. 5 show that a maximum iron content of the deposit is actually attained with solutions containing a small proportion of iron, but with the other solutions this condition is not reached even at a *C.D.* of 5 amps./dm.<sup>2</sup> Diffusion of the ions is so rapid at 90° that depletion of the electrolyte near the cathode probably does not occur to any appreciable extent; this is in agreement with the fact that the curves show that there is no tendency for the proportion of iron in the deposit to decrease once the maximum has been reached. The deposit at 90° does not ever appear to contain a much higher proportion of iron than does the electrolyte and hence the influence of diffusion cannot be appreciable. It should be mentioned here that there was considerable difficulty in carrying out these experiments at 90° owing to the tendency of the iron to oxidise and precipitate; the results must therefore not be regarded as being exactly reproducible.

### Summary.

- (1) The investigations already made of the compositions of the alloys deposited from well buffered solutions of definite hydrogen ion concentration containing various mixtures of ferrous and nickel sulphates at a series of *C.D.*'s have been extended to higher temperatures.
- (2) The general conclusion already arrived at that the relative tendencies for iron and nickel to deposit in the form of an alloy is independent of the hydrogen ion concentration of the electrolyte has been confirmed.
- (3) At higher temperatures the rate of increase of the proportion of iron in the deposit with increasing *C.D.* is much less than at ordinary temperatures; this is in agreement with a prediction based on electrodeposition potential measurements.
- (4) The initial deposits and those containing the maximum amount of iron contain less iron at 53° than do those obtained from the same solutions at 15°.
- (5) The influence of dilution and stirring at 53° is similar to that observed at ordinary temperatures, but it is not so marked on account of

<sup>4</sup> Cf. Creutzfeldt, *Z. anorg. Chem.*, 1921, 121, 25.

the increased rate of diffusion at the elevated temperature. The effect of diffusion is almost negligible at 90°.

(6) There is a minimum iron content of the electrolyte from which the initially deposited alloy contains relatively less iron than does the electrolyte. This minimum is decreased as the temperature is increased, probably owing to the decreased retarding effect of iron on stable nickel deposition at increased temperatures.

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## AN ACCURATE METHOD FOR COMPARING THE COMPRESSIBILITIES OF GASES BELOW ATMOSPHERIC PRESSURE.

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(Received 17th April, 1928.)

The most reliable of the physico-chemical methods of determining the exact molecular weights of gases is based on Berthelot's principle of limiting densities which assumes that the law of Avogadro is strictly valid only at very low pressures. The ratio of the densities of rarefied gases should hence approximate the more closely to the true molecular weight ratio the lower the pressure at which the comparison is made. The experimental determination of gaseous densities however at pressures no lower than 200 mms. presents great difficulties when a degree of accuracy as great as 1 part in 10,000 is demanded, and this limit must be attained if the final values are to serve as a check to the purely chemical methods of atomic weight determination. Moreover at this pressure the deviations even of the permanent gases from the gas laws are still appreciable. The procedure followed by most investigators has been first to measure the densities at standard conditions of temperature and pressure and then to find the factor necessary to convert these to limiting densities by determining the deviations from Boyle's law at 0° C. over a suitable pressure interval from 1 atmosphere downwards. This gets over the difficulty of weighing gases accurately at low pressures but presupposes (a) that the error in the compressibility measurements is sufficiently small, and (b) that from these measurements the limiting value of  $PV$  (*i.e.* the value of  $PV$  at 0° C. at infinitely low pressures) can be calculated with the required precision.

An examination of the accuracy attained in recent investigations shows that (a) may be questioned;—for the individual values of  $1 + \lambda$  exhibit a lack of concordance which in many cases notably exceeds the error of measurement. An example of this is the factor ( $1 + \lambda$ ) for oxygen itself to which attention has been drawn by the German Atomic Weight Commission.<sup>1</sup> The most probable mean values for this coefficient obtained by three independent sets of workers show a maximum divergence of 1 part in 8300 but the individual values often exhibit discrepancies as large as 1 part in 2500. Again the extreme values in the recent series of determinations of the compressibility of nitrogen carried out by Moles and Clavera<sup>2</sup> differ by

<sup>1</sup> *German At. Wt. Comm. Report*, 1926; *Ber.*, 1926, **59**, 1; *ibid.*, 1927, **60**, 1; *ibid.*, 1928, **61**, 1.

<sup>2</sup> Moles and Clavera, *Z. anorg. Chem.*, 1927, **167**, 49.

1 part in 2000, though for this gas the mean values obtained by various investigators agree very closely with each other. When it is considered that all compressibility determinations of the permanent gases with the exception of those of Baxter and Starkweather<sup>3</sup> have been made by closely similar methods the question may well be asked whether the agreement recorded can be taken as a criterion of their accuracy.

Supposition (b) is open to criticism since no  $PV$  measurements of high precision have been carried out below a pressure of 200 mms.

It is true that the experimental data for the permanent gases show that  $PV$  is a linear function of  $p$  to a close approximation between the pressure limits of 1 and 0·2 atmosphere. Further it is probable on theoretical grounds that the isotherms are straight lines to much lower pressures. But it is at least unsatisfactory that no attempt has been made to bridge this gap and that the values of  $1 + \lambda$  can only be deduced by extrapolation over a comparatively large interval.

These considerations suggest that if physico-chemical methods are to rank with the classical methods in the calculation of fundamental atomic weights more complete and more accurate data for the compressibility coefficients of the permanent gases is necessary.

Some years ago it occurred to one of us that considerable advantages could be gained by comparing the compressibilities of gases in a differential apparatus instead of measuring them separately in the orthodox way. It seemed likely that this plan would go far to eliminate any constant errors inherent in the usual procedure. The idea in mind was to start with equal volumes of the two gases at the same pressure, expand them by known amounts until the pressures were again equal and so by repeating the process to compare the volumes at a series of equal pressures.

It was thought that this would be easy to realise experimentally by connecting two similar cylindrical volumeters containing the gases confined over mercury with two dead spaces forming the upper extremities of a short mercury manometer. The total space filled by gas being adjusted to equality as nearly as possible on both sides of the manometer and the pressures made identical, it would be easy to withdraw accurately known volumes of mercury from the volumeters and so expand the gases until they were again exerting equal pressures. By this system the accuracy of the results would be limited mainly by the accuracy of setting of the manometer points, the errors in the calibration of the dead space and connecting tubes, and the error in weighing mercury withdrawn from the cylinders, provided that the whole apparatus could be kept at a constant temperature. This on account of its compact form and the absence of long manometric columns was fairly easy to manage.

After much preliminary work an apparatus on this principle was set up, the details of which are shown in Fig. 1 and the working of which will now be described.

The essential parts of the apparatus are shown in the figure.

The variation of the volumes of the gases was carried out in the two stout glass cylinders A and B, by the withdrawal of mercury through the taps D and G. Each cylinder or volumeter was joined to one arm of the differential point manometer ab. The volumes of the dead spaces x and y and of the capillary connections defined by the marks mno on one side, and pqr on the other, were calibrated before the apparatus was set up. The three-way taps C and H served first to introduce the gases into each side, after which

<sup>3</sup> Baxter and Starkweather, *Proc. Nat. Acad. Sci., U.S.A.*, 1925, 11, 231; 1926, 12, 20, 699, 703; 1928, 14, 50, 57.

mercury was run from the other branch of each tap to  $m$  on one side and  $n$  on the other. The volumes of gas on each side were therefore defined by the calibrated volumes  $mnox$  and  $rppq$  plus the volumes of mercury withdrawn from A and B which were filled at the start to  $n$  and  $q$ .

The equality of pressure of the two gases was indicated by the point manometer  $ab$  which was adjusted prior to each experiment, so that the points were set simultaneously with equal pressure on each side.

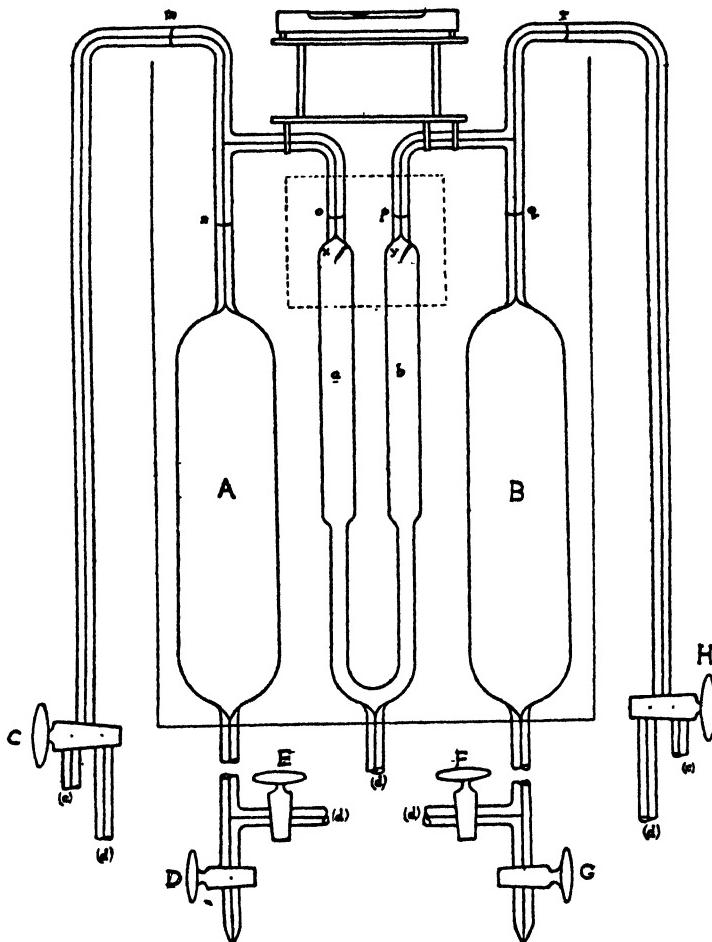


FIG. 1.—Leads marked (c) communicate with apparatus for preparation of gases.  
(d) are provided with gas traps, rubber hose and mercury reservoirs.

A suitable quantity of mercury was then allowed to run out from each cylinder and the pressure again adjusted to equality by removing small increments of mercury until an exact point setting was attained. From the weights of mercury withdrawn at each operation the ratio of the volumes of the two gases at equal pressure was calculated which was clearly identical with the  $\rho V$  value of the one gas divided by the corresponding  $\rho V$  value of the other. The series of ratios thus obtained were plotted against the corresponding pressures and extrapolated to zero pressure, and from the slope of

the graph the relative compressibility of the gases compared was determined. Using the customary notation where  $\frac{P_0 V_0}{P_1 V_1} = 1 + \lambda$  for the deviation from Boyle's law of a gas between the pressure limits of 1 and 0 atmospheres, this procedure gave a value for  $\frac{(1 + \lambda)_A}{(1 + \lambda)_B}$  i.e., the ratio of the compressibility coefficients of the gases A and B.

It was necessary only to know approximately the absolute pressures for the  $(PV)/P$  diagram, and these pressures were found from the initial pressure, and the measured increase in volume assuming Boyle's law. It should be pointed out that this method really amounts to plotting the ratios of  $(PV)$  against  $1/V$ . In the case of the permanent gases, however, this does not lead to results appreciably different from the plotting against pressure.

The volumeters, which were of about 300 c.c. capacity, and the manometer were mounted side by side and close together on a stout wooden stand which had previously been waterproofed. The manometer attached to the same stand was placed symmetrically in front of the cylinders. The apparatus was set up inside a large metal tank provided with a plate-glass front. The capillary leads for the manometer and for the introduction and withdrawal of mercury from the cylinders passed through holes in the bottom of the tank and in the stone bench on which the apparatus was set up, and the taps D, E, F, and G were mounted on a stand fixed to the floor about 80 cm. below the base of the tank.

In order that the points could be set and the heights of the mercury meniscuses measured when the bath was filled with ice, the dead spaces were surrounded on all sides except the front where they were close to the glass by a cage made of copper gauze. The points were illuminated by a Pointolite lamp. A parallel beam from this passed down the vertical part of a metal elbow-joint, which was fitted with a mirror at the angle. This reflected the beam to a ground glass window at the end of the horizontal part; which passed through a hole in the back of the gauze cage so that the window was just behind the dead spaces.

Preliminary experiments showed that slight temperature variations in the tank were apt to occur on standing, especially in the vicinity of the dead spaces. To obviate this a circulator was arranged which delivered water from another vessel containing ice into the tank and kept its contents continually stirred. This arrangement proved very satisfactory.

It was found unfortunately that the apparatus shifted slightly in the course of an experiment so that if it was adjusted for both points to be set simultaneously with equal pressure on each side, this equality was not always maintained to the end of an experiment. In order to overcome this difficulty a delicate spirit level was fixed on a platform with three V-grooves which rested on the horizontal portions of the capillary tubes joining each limb of the manometer to the corresponding volumeter. At the commencement of each experiment the points were arranged to set simultaneously with equal pressure on each side. This adjustment was made by means of a levelling screw on the stand supporting the tank. The spirit level which was provided with its own levelling screws was then adjusted to a zero position. It was kept in this position by adjustment of the levelling screw on the stand supporting the tank during the experiment. In all cases, the setting of the points with equal pressure on each side was tested at the end of the experiment. The error was in most cases negligible, but in two

cases was appreciable. The results of these two experiments showed deviations in the direction and to extent indicated by this and were accordingly discarded.

The change of volume of the volumeters with change of pressure was measured. It was found to be exactly the same on each side (22·4 cu. mm. per atm.). In view of this equality it was assumed that the changes of volume by distortion due to varying weights of mercury in the volume bulbs would also be the same on the two sides.

### Calibration of Dead Spaces, etc.

The dead spaces in the tubes used for the manometer were calibrated in the usual way by weighing mercury run out from the tube after setting to a mark on the capillary just above the dead space ( $\sigma$  and  $\rho$  for the two dead spaces in the figure), and after setting to the point in each tube. The difference gave the volume of the dead space. The temperature was maintained approximately constant by the use of a large water-bath, in which the whole tube was immersed during calibration.

The only departure from the usual practice was the measurement of the height of the mercury meniscus at each setting to the point. In a series of calibrations without this refinement variations as high as 20 cu. mm. occurred, and it was found quite impossible to get consistent results. When the height of the meniscus was allowed for satisfactory results were obtained. The height of the meniscus was measured by means of a horizontal reading microscope, the tube being set up close to a plate-glass window in the water-tank.

The corrections for the variation of dead space volume with meniscus height were made from values found by Mr. Sever who has made careful measurements of the volume of a mercury meniscus at heights between 0·8 and 2·5 mm. These results are unpublished and the authors are much indebted to Mr. Sever for them.

The capillary connecting tubes ( $mno$  and  $pqr$  in the figure) were calibrated after the assembly of the volume-bulbs and manometer. These, mounted on the wooden stand, were inverted, and taps were sealed on beyond  $m$  and  $r$ . Mercury was adjusted simultaneously to two marks ( $n$  and  $\sigma$  on one side, and  $p$  and  $q$  on the other) by tilting the whole stand until they were on the same level, and run out to the third mark on each side.

The complete calibration results are given on p. 383.

### Experimental Procedure.

The whole apparatus was evacuated via the taps C and H before each experiment. The bath was filled with crushed ice and water, and the volume bulbs filled with mercury. The mercury was set exactly to the marks  $n$  and  $q$  after standing in the ice bath about an hour. The water circulator was then set going and the adjustment of the points to exactly equal level together with the setting of the spirit-level bubble to a zero position was carried out.

About 50 c.c. of mercury was then run out from each side through D and G into tared vessels. The gases were now introduced into each side via C and H. After the gases had been introduced into each side to nearly equal pressure (about 1 atmosphere), threads of mercury were brought through the other branches of the taps C and H to  $m$  and  $r$ . The whole was then left to attain 0° C. for at least 2 hours, after which the mercury

was reset exactly to  $m$  and  $r$ . Small quantities of mercury were then run from the volume bulbs into the two tared vessels used for the first 50 c.c. until the manometer was exactly set, and at this stage the meniscus heights of the mercury in the arms of the manometer were measured. These readings gave the first volume ratio. A further series of ratios at almost the

#### CALIBRATION OF DEAD SPACES.

Diameter of manometer tubes, 19·6 mm.

The following corrections were applied to the dead space volume.

Height of meniscus . . . . . 1·0 1·1 1·2 1·3 1·4 1·5 mm.

Vol. change per 0·1 mm. height change 8·6 8·25 7·9 7·55 7·2 cu. mm.

Height of meniscus . . . . . 1·5 1·6 1·7 1·8 1·9 2·0 mm.

Vol. change per 0·1 mm. height change 6·85 6·5 6·15 5·8 5·45 5·1 cu. mm.

First Space; Vol. to Point.			Second Space; Vol. to Point.		
Vol. (c.c.)	Men. Height (mm.)	Corr. Vol.	Vol. (c.c.)	Men. Height (mm.)	Corr. Vol.
29·5001	1·63	29·5093	29·0012	1·60	29·0081
29·5015	1·62	29·5096	29·0046	1·48	29·0031
29·5190	1·40	29·5121	29·004	1·60	29·0076
29·5121	1·51	29·5132	29·0073	1·56	29·0117
29·5186	1·39	29·5111	29·0132	1·47	29·0115
29·5184	1·44	29·5139	29·0145	1·46	29·0110
29·5157	1·44	29·5114	29·0076	1·48	29·0061
29·5158	1·43	29·5108	29·0097	1·48	29·0085
			29·0016	1·60	29·0088
	Mean,	<u>29·5114</u>	29·0123	1·44	29·0083
			29·0048	1·57	29·0098
			29·0020	1·54	29·0048
			29·0081	1·51	29·0092
			29·0061	1·58	29·0120
			29·0121	1·46	19·0092
			29·0086	1·56	29·0132
			Mean,	<u>29·0093</u>	
Volume to Mark.			Volume to Mark.		
	31·8843 c.c.			31·3124 c.c.	
	31·8825			31·3122	
	31·8832			31·3124	
	31·8827			31·3122	
Mean,	<u>31·8832</u>		Mean,	<u>31·3123</u>	
	<u>29·5114</u>			<u>29·0093</u>	
	<u>2·3718</u>			<u>2·3030</u>	
Vol. of Capillary Connections.			Vol. of Capillary Connections.		
	0·2600 c.c.			0·2480 c.c.	
	0·2601			0·2481	
	0·2602			0·2483	
Mean,	<u>0·2601</u>		Mean,	<u>0·2481</u> c.c.	
Total dead space volume.			Total dead space volume.		
	2·632 c.c. for meniscus height 1·50 mm.			2·551 c.c. for meniscus height 1·50 mm.	

same pressure was obtained by running out very small quantities of mercury from one or both volume bulbs into weighed tubes, the mercury in the manometer being lowered and brought up again to the points, which were set again, the meniscus heights being read at the same time.

This procedure was repeated, running out large and small quantities of mercury, so that volume ratios were obtained at about eight pressures from atmospheric down to about 150 mm. pressure. At each pressure from three to eight readings were taken.

During the series of settings at the highest pressure the actual pressure of the two gases was found by comparing the height of the mercury when set to the points with that of the mercury reservoir, and reading the barometric height.

During an experiment the spirit-level was kept at the same indication as at the start by adjustment of the screw supporting the base of the tank. At the end of the experiment the equality of level of the points was tested by lowering the mercury from the capillary cut-offs and opening C and H to the Töpler pump, which put the two dead spaces of the manometer into communication, and testing the setting.

The vessels of mercury were weighed with a possible maximum error of 5 mgm., for the quantities corresponding to the higher pressures. For the much larger quantities corresponding to the two or three lowest pressures there was a possible maximum error of about 15 mgm.

### Calculation of Results.

From the weights of mercury withdrawn the volumes were calculated. Addition of each volume increment to the total volume previously withdrawn plus the volume of the capillary connections and dead space (for a meniscus height of 1.5 mm.), gave a series of uncorrected total volumes. Two series were obtained corresponding to the two gases. Each uncorrected volume was corrected for change of volume of the volumeter with change of pressure, and for change of volume of the dead space with meniscus height.

The ratio of each corrected volume on one side to the corresponding corrected volume on the other was then found. Some 25 to 40 ratios were thus obtained in groups of from 3 to 8 ratios, each group corresponding to one of 7 to 10 pressures between atmospheric and 100 mm. The mean of each group was plotted against the corresponding pressure, which was found from the pressure measured at the start of each experiment and the increase in volume, assuming Boyle's law. By extrapolation the value of the ratio at zero pressure was found. This ratio divided by the ratio at a pressure of 760 mm., gave the value of  $\frac{(1 + \lambda)A}{(1 + \lambda)B}$ . Linear extrapolation to zero pressure was always adopted as the results showed no evidence of departure from this.

No vacuum corrections were made for the weighings as these would cancel out for the two sides at every step.

### Preparation of the Gases.

*Hydrogen.*—This was prepared by the electrolysis of baryta solution. It was passed over solid potash and phosphorus pentoxide, and through a charcoal tube cooled in liquid air. This is probably the best method of preparing pure hydrogen, excepting diffusion through palladium.<sup>4</sup> The

<sup>4</sup> Burt and Edgar, *Phil. Trans. Roy. Soc.*, 1916, A 216, 413.

gas was stored in a tube of palladium sponge, affixed to the apparatus by a ground joint, and driven off as required by heating. As it was possible that the palladium sponge might have retained traces of moisture, although it was evacuated at  $150^{\circ}$  and washed out several times with hydrogen, a tube of phosphorus pentoxide was interposed between the storage tube and the apparatus.

*Oxygen.*—This was prepared in the usual way from pure potassium permanganate. It was passed over liquid and solid potash and phosphorus pentoxide. It was then liquefied and the middle fraction used for the determination.

### Results.

#### Tests with Hydrogen.

Three experiments were carried out with hydrogen in both volume-bulbs. Below the results are given, in full for one experiment, only the mean ratios at each pressure being given for the other two.

Experiment 1.										
Pressure . . .	800	680	570	500	400	310	220	190	160	mm.
Mean vol. ratio	1.05932	29	27	27	32	30	33	31	28	
Experiment 2.										
Pressure . . .	710	590	530	460	410	350	280	210	170	mm.
Mean vol. ratio	'99120	26	26	20	25	29	27	22	27	
Individual ratios	10, 14	30, 26	22	21	26	33	26	21	30	
	17, 31	23, 25	26	19	26	30	28	21	32	
	26	24	30	20	24	26	28	24	18	
Experiment 3.										
Pressure . . .	740	660	580	470	390	310	230	170	140	mm.
Mean vol. ratio	1.02243	46	41	47	45	42	41	42	(34)	

The resulting values of the ratio of the value of  $(1 + \lambda)$  for the gas on one side to its value for the gas on the other were :—

$$\begin{aligned} \text{Expt. 1;} & \quad 1.00000 \\ \text{Expt. 2;} & \quad 1.00005 \\ \text{Expt. 3;} & \quad 0.99995 \end{aligned}$$

$$\text{Mean } \underline{1.00000}$$

In the case of experiment 3, the final volume ratio shown in brackets in the table was omitted from the calculation of the result. It was discordant from the other points in the series, and no weight was attached to it because at the close of that experiment it was necessary to work in haste, and only one setting of the manometer was made. In experiment 1 no point differed by more than 1 part in 25,000 from the mean line, the error in experiment 2 being 1 in 17,000, while in experiment 3, excepting the point omitted was 1 part in 25,000. In each case the mean line was straight and was worked out by the method of least squares.

It is considered that these test results may be regarded as good evidence of the absence of constant errors.

#### Hydrogen and Oxygen.

In all eight experiments were carried out in which the compressibilities of hydrogen and oxygen were compared. Two of these (expts. 2 and 5) were discarded owing to shift in the manometer as has been previously mentioned. The results of two more (nos. 6 and 7) were rendered slightly uncertain owing to accidental loss of mercury.

The results of the remaining four are given below as in the case of hydrogen:—

Experiment 1.											
Pressure . . .	750	689	620	540	447	373	289	223	180	137	
Mean vol. ratio	1.01184	200	205	216	234	255	275	286	297	306	
Experiment 3.											
Pressure . . .	747	658	568	474	393	302	217				
Mean vol. ratio	1.02049	662	681	700	713	729	745				
Experiment 4.											
Pressure . . .	708	623	531	464	398	329	278	233			
Mean vol. ratio	1.03651	667	685	707	711	747	758	(776)			
Experiment 8.											
Pressure . . .	730	657	534	454	360	257	198	140			
Mean vol. ratio	0.98984	998	925	940	961	981	988	103			

These results again show no evidence of departure from a straight line and the values of  $\frac{(1 + \lambda)O_2}{(1 + \lambda)H_2}$  were worked out by the method of least squares.

The value shown in brackets was the only one in the last three experiments which was more than 1 part in 20,000 different from its mean line. The error on this point was about 1 part in 9000 and as this point, being at the lowest pressure would be the most likely to be in error it was given no weight in the calculation of the mean line. In the first experiment the points were slightly less concordant, the maximum deviation from the line being about 1 in 15,000.

The values of the compressibility ratios are given below:—

Experiment.	Ratio.
1	1.00150
3	1.00137
4	1.00152
8	1.00153
6	1.0015(4)
7	1.0015(0)
Mean	<u>1.00148</u>

The value of the compressibility coefficient of oxygen has been discussed by Moles<sup>5</sup> who gives 1.00091 as the most probable value. The following are the determinations of  $(1 + \lambda)$  for hydrogen, which have been made at 0°C.

Chappuis <sup>6</sup> . . .	0.99942
Jaquerod and Scheuer <sup>7</sup> .	0.99947
Guye and Batuecas <sup>8</sup> .	0.99935
Mean	<u>0.99942</u>

This leads to the value 1.00149 for the ratio of the compressibility coefficients of oxygen and hydrogen, in very good agreement with the value obtained by us.

Burt and Edgar<sup>4</sup> found the ratio of the combining volumes of oxygen and hydrogen to be 2.00288 to 1. From this the ratio of the compressibility coefficients should be 1.00144, a value rather lower than that found here.

<sup>5</sup> Moles, *Z. anorg. Chem.*, 1927, 167, 40.

<sup>6</sup> Chappuis, "Nouvelles études sur les Thermomètres à gas," *Trav. et. Mem. du Bur. Intern.*, I3.

<sup>7</sup> Jaquerod and Scheuer, *Mem. Soc. Physique Genève*, 1908, 35, 659.

<sup>8</sup> Guye and Batuecas, *J. Chim. Physique*, 1922-3, 20, 322.

It is evident from the foregoing that the method is capable of giving results of a high degree of accuracy, indeed the deviation of the points from the mean line in the individual experiments leaves little to be desired. The values for the ratios in five of the six experiments are closely concordant, but the lower value obtained in experiment 3 is difficult to explain. It has been included in calculating the final mean since there is no valid reason for its rejection.

Experience gained during the investigation has brought to light various sources of error of which the most important are (*a*) the slight displacement of the relative position of the manometric points due to lack of rigidity in the apparatus, and (*b*) a possible uncertainty in the correction made for the change of volume in the dead spaces with meniscus height. In the calibration these heights did not vary over as great a range as in the actual experiments and this may have introduced a slight error.

The investigation is regarded as an attempt to develop a new high precision method of comparing compressibility coefficients, and in view of the encouraging results obtained a fresh apparatus is under construction with which it is hoped to obtain data for a number of gases.

We wish to express our thanks to the Department of Scientific and Industrial research for its assistance which enabled one of us to devote time to the work.

### Summary.

A new differential method for the measurement of compressibility has been developed.

The principal advantages of the method used are (1) its compactness, rendering temperature control easy, (2) the elimination of constant errors, and (3) increased accuracy of volume measurement resulting from making correction for variation of dead space volume with meniscus height.

The ratio of the compressibility coefficients of hydrogen and oxygen has been measured.

$$\text{The value found was } \frac{(1 + \lambda)\text{O}_2}{(1 + \lambda)\text{H}_2} = 1.00148.$$

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## THE HARDNESS OF ELECTRO-DEPOSITED NICKEL.\*

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(Received 2nd May, 1928.)

In recent years a number of investigations have been made which have contributed to a fuller understanding of the process of electro-deposition of nickel. Improved methods for the control of the conditions of deposition have been introduced, and some knowledge has been acquired concerning the influence of constituents frequently used in depositing solutions upon the nature of the deposit. Precise knowledge, however, as to the actual internal structure and physical properties of deposits produced under

\* Communication from the Research Department, Woolwich.

definite conditions of deposition is still very meagre owing to the difficulty of applying quantitative tests to deposits of the thickness ordinarily produced.

One object of the present investigation has been to develop practical methods of determining hardness and stress in deposits and to ascertain the value of such tests for the control of conditions of deposition for the production of deposits for specific purposes. A further object has been to study by means of these tests the properties of deposits obtained under conditions from which impurities ordinarily present have been almost entirely eliminated. The experimental work has consisted mainly in the production of nickel deposits under carefully controlled conditions (varied according to a definite scheme as regards composition of bath, temperature, purity of anodes etc.), and the subsequent testing of the deposits.

### **Methods of Determining Hardness and Stress in Electro-Deposited Metals.**

#### **i. Hardness.**

(a) *Scratch Methods.*—Scratch hardness tests have been frequently applied to electro-deposited metals. In the usually adopted scratch test the specimen is moved horizontally under a diamond or sapphire scratching point which is pressed by a definite load into the surface of the specimen. The degree of hardness is indicated by the fineness of the scratch produced.

A serious disadvantage of this test is the difficulty of obtaining comparable results by different scratch testing instruments. Even with a single instrument, considerable wear of the cutting edges of the scratching point occurs during use so that re-calibration is necessary from time to time. A further drawback is the very slight change in the width of scratch which corresponds to a large change in hardness.

(b) *Indentation Methods.*—The Brinell Test and the Scleroscope Test are widely used for determining the indentation hardness of metals, but up to the present have not been extensively applied to electro-deposited metals. These two tests do not measure identical properties of a metal. The Brinell Hardness Test is the more accurate and yields results which are practically free from instrument error. For this reason it is to be preferred to the scleroscope test, and its use by different workers in the investigation of the hardness of deposits is likely to be more valuable than the hitherto more popular scratch test.

For the accurate determination of the Brinell Hardness of a deposited metal, it is important that the test should not be affected by the hardness of the basis metal. Results of experiments by Moore<sup>1</sup> on the accuracy of the Brinell test as applied to thin specimens suggest that in order to ensure the elimination of the influence of the basis metal the thickness of the deposit for testing should be at least seven times the depth of the Brinell ball impression formed in the test, although large errors are not as a rule introduced unless the ratio is considerably smaller. Calculated upon the basis of a ratio of 7 : 1, Table I. shows the minimum thickness of deposits that can be accurately tested for Brinell Hardness by a 1 mm. ball with 10 kg. load. It is not possible to lay down a rule under which reasonably accurate tests may be obtained with a smaller ratio of thickness of deposit to depth of impression; the relative hardness of deposit and basis metal, as well as other factors, enter into the question.

<sup>1</sup> "Investigation on the Brinell Method of Determining Hardness." H. Moore  
Proc. International Assoc. for Testing Materials, 1909.

TABLE I.—LIMITING THICKNESS OF DEPOSIT FOR THE BRINELL HARDNESS TEST WITH 1 MM. BALL AND 10 KG. LOAD.

Brinell Hardness Number.	Diameter of Impression. Mm.	Depth of Impression.		Minimum Thickness of Deposit.	
		Mm.	Ins.	Mm.	Ins.
100	.351	.0319	.00125	.223	.0087
125	.315	.0255	.00110	.178	.007
150	.288	.0212	.00084	.150	.0059
175	.267	.0182	.00072	.127	.0050
200	.250	.0159	.00063	.111	.0044
250	.224	.0127	.00050	.089	.0035
300	.205	.0106	.00042	.074	.0029
400	.178	.0080	.00031	.056	.0022
500	.159	.0063	.00025	.044	.0017
600	.145	.0053	.00021	.037	.0015

The approximate range of the Brinell Hardness number of nickel deposits is 130-450, so that the minimum thickness suitable for testing with 1 mm. ball and 10 kg. load ranges from .002 to .007 inch.

For testing thinner deposits with a 1 mm. ball a lighter load than 10 kg. may be used, but further investigation is required into tests made under these conditions in order to determine suitable methods of preparing the specimens and to establish the comparability of results with those obtained using a 10 kg. load.

In the present investigation deposits 0.01 in. in thickness have been prepared for the determination of Brinell Hardness with a 1 mm. ball and 10 kg. load.

## 2. Stress.

In the method developed by Kohlschütter and his associates<sup>2</sup> for the determination of the stress in a deposit, the amount of bending of a strip of platinum that occurred when the deposit was formed on one side only of the strip was measured and taken as an indication of the intensity of the stress.

The authors have found it more convenient and reliable in applying stress tests to nickel deposits to replace platinum strip by hardened and tempered steel strip. A number of strips of hardened and tempered spring steel 0.2 in. wide 0.016 in. thick were obtained from the same consignment. This material was remarkably uniform in its elastic properties. In each test two strips each 6-in. long were cleaned cathodically in alkali to remove grease and then anodically in 25 per cent. sulphuric acid for 30 seconds. They were then dried in a hot air bath and clamped together back to back in the manner shown in Fig. 1b and the distance between the tips measured. The strips were then weighed and stopped off with collodion varnish so as to leave a depositing surface of 4 ins. on one side only of each strip. The ends of the two strips were inserted into a clamp in the manner shown in Fig. 1a and, thus held, cleaned anodically in 25 per cent. sulphuric acid for exactly 30 secs. at 200 amperes per sq. ft., washed in water and introduced into the depositing bath. The loss in weight caused by the anodic cleaning was small and was found to be constant over a number of experiments. The strips were then plated with nickel under the particular conditions being

<sup>2</sup> "Application of Contractometer to the Study of Nickel Deposition." E. A. Vuilleumier, *Trans. Amer. Electrochem. Soc.*, 1922, 42, 99.

investigated, for a time calculated to produce a deposit .0005-in. thick. The stopping off varnish was subsequently removed by soaking the strips in acetone. After drying the strips were weighed and the increase in the distance between the tips when the strips were clamped back to back as in Fig. 1b was measured. The strips were then immersed in boiling water for one hour, after which the distance between the tips was again measured. Constant reproducible results could only be obtained in this way as movement indicating an increase in the stress in the deposits continued after their removal from the nickel bath, and until the strips were treated in boiling water. The weight of nickel enabled a determination of the average thickness of the deposit to be obtained.

The results in each case recorded are expressed as the amount of movement of one strip in mm. for a deposit .0005-in. thick.

### The Influence of Composition, Temperature, etc., of Electrolyte on Hardness and Stress in Electrodeposited Nickel.

#### I. Previous Work.

In a previous investigation by one of the authors<sup>3</sup> the Brinell Hardness Numbers of a series of deposits formed in a typical plating solution containing nickel sulphate and ammonium sulphate were contrasted with the Brinell Hardness Numbers of a series of deposits formed in a typical plating solution containing nickel sulphate and boric acid.

The composition of these solutions and the results obtained in the experiments are shown in Table II.

TABLE II.—HARDNESS OF NICKEL DEPOSITED FROM SOLUTIONS CONTAINING (1) BORIC ACID; (2) AMMONIUM SULPHATE.

(Extracted from previously published paper).<sup>3</sup>

*Electrolytes.*—N Bath—240 g. Nickel sulphate (cryst)  
15 g. Sodium chloride } per  
30 g. Boric acid.      litre.  
Y Bath—66·5 g. Nickel sulphate (cryst)  
21 g. Ammonium sulphate } per  
8 g. Potassium chloride      litre.

$\text{p}_\text{H}$ Range 5·8-6·0. N Bath { Temperature 18°-22° C. Average Thickness 0·08 In.	$\text{p}_\text{H}$ Range 5·6-5·8. Y Bath { Temperature 17°-21° C. Average Thickness 0·03-0·06 In.
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No.	Current Density Amps. p. Sq. Ft.	Brinell Hardness Number.	Remarks.	No.	Current Density Amps. p. Sq. Ft.	Brinell Hardness Number.	Remarks.
N <sub>31</sub>	5	181		Y <sub>4</sub>	5	385	
N <sub>32</sub>	10	186		Y <sub>5</sub>	10	352	
N <sub>33</sub>	15	217		Y <sub>7</sub>	10	358	
N <sub>1</sub>	20	231		Y <sub>8</sub>	10	389	
N <sub>3</sub>	20	214		Y <sub>10</sub>	10	420	
N <sub>6</sub>	20	210	Very tough; smooth surface.	Y <sub>6</sub>	15	376	Fairly smooth; somewhat brittle.

The results showed a striking difference in the Brinell Hardness of the deposits from the two solutions. The hard deposits were found to have a

<sup>3</sup> "Hardness of Electrodeposited Iron, Nickel, Cobalt and Copper." D. J. Macnaughtan, *J. Iron and Steel Inst.*, 1924, 109, 409.

finer crystalline structure and a higher tensile strength than the soft deposits. The tensile strength of the hard deposits ranged from 70-80 tons per sq. inch with 2-5 per cent. elongation, while the soft deposits broke at about 25-30 tons per sq. inch with an elongation of 30-35 per cent. Subsequent experience showed that the deposits with the higher Brinell Hardness were more difficult to machine and had greater resistance to wear than deposits having lower Brinell Hardness.

In consequence of these results the solution containing ammonium sulphate has since been used for the production of hard although somewhat brittle deposits for purposes where high resistance to wear was essential, and the solution containing boric acid has been used for the production of softer but more ductile deposits which were more suitable for purposes where resistance to wear was of less importance.

## 2. Influence of Temperature.

In the earlier series of experiments in the present investigation the solutions were maintained during deposition at 20° C., the current density used being 15 amperes per sq. foot. At this temperature the nickel from both solutions was deposited in a highly stressed condition, so that during the formation of thick deposits (up to 0.1 inch) stripping from the cathode could only be avoided by taking extreme care to secure high adhesion to the cathode surface. Even when this was done fine cracks were occasionally found in the hard type of deposit, indicating local failure under stress.

The effect of increasing the temperature of the solutions in order to reduce the stress in the deposits was investigated by the method already described. The highest practicable limit of temperature for the solutions was 35° C. owing to the comparatively low melting-point of the wax mixture used for stopping off parts of the articles treated in the solutions. The effect of temperature of deposition upon the stress in the deposits is shown in Fig. 2. In view of the considerable reduction in stress secured by raising the temperatures of the solutions up to 35° C. it was decided to adopt this temperature. Brinell Hardness tests made on deposits produced at 20° C. and at 35° C. indicated that the reduction in hardness was relatively less than the reduction in stress. Some results of hardness tests are shown in Table III.

It was subsequently found that with these two typical solutions operated at 35° C. thick deposits of hard or soft nickel free from internal cracks could be readily obtained.

At the higher temperature owing to the greater solubility of the nickel salts it was possible to increase the amount of nickel sulphate in the solution containing ammonium sulphate and thereby raise the permissible rate

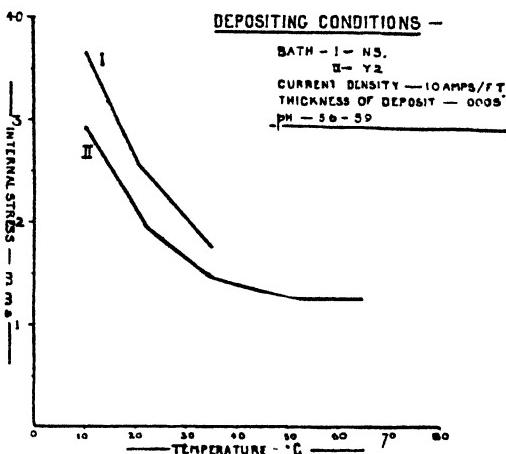


FIG. 2.—Effect of temperature upon internal stress in nickel deposits.

of deposition. The solution Y<sub>4</sub> finally adopted for the production of hard deposits had the composition given in Table V., while Table III. shows the hardness of a typical deposit from this solution.

TABLE III.—EFFECT OF TEMPERATURE OF DEPOSITION ON HARDNESS OF DEPOSITED NICKEL.

*Depositing conditions.*—Current density, 15 amps./sq. ft.,  $p_H$  range 5·6-6·0.

Reference No.	Bath. (See Table V.)	Temperature.	Brinell Hardness Number 1 mm. Ball 10 kg. Load.
T 41	Y 2	20° C.	390
T 38	Y 2	35	328
T 40	Y 4	20	374
T 37	Y 4	35	315
T 42	N 5	20	209
T 39	N 5	35	158

### 3. Preparation of Nickel Sulphate of High Purity.

For the purpose of ascertaining which factor or factors were responsible for the marked difference in the hardness of deposits indicated in Table II. it appeared to be essential in the first instance to prepare solutions and anodes which would be as free as possible from impurities since these might influence the properties of the deposits.

The nickel sulphate available was found to contain perceptible amounts of iron, copper, and zinc. For its purification, after some investigation, the following method was adopted. To a solution of the salt sufficient pure hydrogen peroxide was added to oxidise the iron present, and the solution was then boiled with some specially prepared pure nickel carbonate. Under these conditions the iron present was precipitated and was subsequently filtered off. It had been claimed<sup>4</sup> that this treatment would simultaneously remove all the copper and zinc present in the solution, but it proved to be more reliable to acidify the filtered solution to  $p_H$  2·5 and while it was still warm to pass sulphuretted hydrogen through it. Traces of copper and zinc present were precipitated as sulphides and then filtered off. Subsequently the solution was concentrated and nickel sulphate of high purity crystallised out. The degree of purity of an average sample of nickel sulphate obtained by this procedure is shown by the following analysis:—

Fe < ·005 per cent., Cu < ·001 per cent., Zn trace, Mn ·001 per cent., Pb < ·005 per cent., Co ·005 per cent.

For the other constituents of the depositing solutions chemicals of A.R. purity were used.

### 4. Preparation of Nickel Anodes of High Purity.

A suitable method for the preparation of nickel anodes of high purity was found to consist in the electrolytic refining of nickel pellets in a solution made from pure salts of the following composition:—

Nickel Sulphate ( $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ )    70 grams }  
Ammonium Sulphate    .    .    21 grams } per litre.  
Potassium Chloride    .    .    25 grams }

<sup>4</sup> "Effect of Impurities in Nickel Salts used for Electrodeposition." M. R. Thompson and C. T. Thomas, *Trans. Amer. Electrochem. Soc.*, 1922, 42, 84.

The nickel pellets were enclosed in a perforated ebonite container. Electrical contact was made with the pellets by means of a platinum spiral. The cathode starting sheets were of platinum foil. The conditions of deposition were as follows :—

Cathode current density 10 amperes per sq. foot.

Temperature of Solution 45° C.  $\rho_H$  6·8-7·0.

The purity of the nickel deposit obtained is indicated by the analysis in Table IV.

TABLE IV.—PURIFICATION OF NICKEL FOR USE AS ANODES.

	Carbon, Per Cent.	Iron, Per Cent.	Copper, Per Cent.	Manganese, Per Cent.	Zinc, Per Cent.	Lead, Per Cent.	Silicon, Per Cent.
Composition of Mond Pellets . . .	0·04	0·008	0·02	0·001	Nil	—	0·015
Composition of Refined Nickel . . .	Nil	0·0015	0·001	0·0004	trace	trace	Nil

### 5. Composition of Solutions used.

The composition of a number of solutions prepared from the salts of high purity are shown in Table V.

TABLE V.—COMPOSITION OF DEPOSITING SOLUTIONS, PREPARED FROM SPECIALLY PURIFIED MATERIALS.

Solution Reference No.	Grams Per Litre.						Remarks
	Nickel Sulphate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ .	Ammonium Sulphate, $(\text{NH}_4)_2\text{SO}_4$ .	Boric Acid, $\text{H}_3\text{BO}_3$ .	Potassium Chloride, $\text{KCl}$ .	Sodium Fluoride, $\text{NaF}$ .	Sodium Sulphate, Anhydrous, $\text{Na}_2\text{SO}_4$ .	
Y <sub>1</sub>	35	21	—	8	—	—	Solutions used for compari- son of the effect of am- monium sul- phate and boric acid (Table VI.)
Y <sub>2</sub>	70	21	—	8	—	—	
Y <sub>3</sub>	70	21	—	19	—	—	
Y <sub>4</sub>	120	21	—	8	—	—	
N <sub>1</sub>	35	—	30	19	—	—	
N <sub>2</sub>	70	—	30	19	—	—	Solutions con- taining so- dium fluo- ride and so- dium sul- phate (Table VII.)
N <sub>3</sub>	70	—	30	8	—	—	
N <sub>4</sub>	120	—	30	19	—	—	
N <sub>5</sub>	240	—	30	19	—	—	
Y <sub>5</sub>	120	21	—	—	10·7	—	
N <sub>6</sub>	240	—	30	—	10·7	—	
N <sub>7</sub>	70	—	30	19	—	213	
N <sub>8</sub>	120	—	30	19	—	213	

As prepared the solutions had a  $\rho_H$  below 5. In order to bring each solution to the required  $\rho_H$  range (5·5-5·9) the following procedure was adopted. A small amount of nickel hydroxide suspension was added and the solution boiled for about 20 minutes, the  $\rho_H$  being thereby brought to a high value. The solution was then allowed to stand over night on a

heated water bath to coagulate the excess of nickel hydroxide. After subsequent filtration the  $\rho_H$  was adjusted to the required range by adding a suitable amount of normal sulphuric acid.

The nickel hydroxide suspension was prepared by adding a boiling solution of purified nickel sulphate to a boiling solution of caustic potash. The hydroxide precipitate was washed by decantation with distilled water and afterwards filtered and further washed until free from alkaline salts. The cake of hydroxide was then transferred to a bottle and shaken into a suspension with distilled water.

#### 6. Details of Deposition Experiments.

For deposition, round glass jars,  $4\frac{1}{2}$  inches in diameter were used each containing one litre of purified solution. The jars were immersed in an electrically heated water bath the temperature of which was thermostatically controlled. Each cathode consisted of a bright rolled mild steel bar  $1\frac{1}{2}$  inch long 1 inch diameter having two flats  $\frac{1}{2}$ -inch wide ground on opposite ends of a diameter and parallel to its axis.

Each cathode, during deposition, was suspended by means of a soldered nickel wire in the centre of a jar while three anodes each approximately  $2\frac{1}{2} \times 1 \times \frac{1}{8}$  inch in dimension were arranged at equal distance around the internal periphery of the jar. The anodes were of highly purified nickel, prepared in the manner described and were hung in the solution from hooks of platinum wire.

The  $\rho_H$  of the nickel depositing solution was determined at intervals by colorimetric methods. Except in the case of the bath containing sodium fluoride and boric acid the acidity of the solution was found to decrease slowly in each experiment so that small additions of normal sulphuric acid were required at intervals in order to keep the  $\rho_H$  of the solutions within the range required.

In order to determine the average anode and cathode efficiencies a copper coulombmeter was connected in series with each nickel bath. The size of the cathode in the coulombmeter was chosen so as to maintain copper deposition at a current density of 10 amperes per sq. foot.

The weight of each nickel deposit was determined by weighing the cathode before and after deposition. The nickel anodes of each bath before use were first boiled in distilled water for about half an hour, to remove any included salts, dried and weighed. After an experiment they were again boiled in distilled water for half an hour, washed and dried. The particles of nickel suspended in the depositing solution and in the water used for washing the anode were collected on a filter, washed, dried and weighed with the anodes. After deposition, the surface of the nickel upon the flats of each specimen was ground down so as to leave a thickness of deposit of 0.1 inch. The ground surfaces were then lightly polished upon fine emery paper and three Brinell Hardness impressions were made near the centre of each flat with a 1 mm. ball under a 10 kilogramme load. Each impression was measured across two diameters at right angles.

For micro-examination the specimens were cut through transversely near the centre and the sections thus obtained were coated with electro-deposited copper in order to protect the edges of the nickel deposit during the grinding and polishing which was subsequently carried out. The polished sections were etched with a mixture of nitric and acetic acids.

The measurement of stress in deposits from the different solutions was determined separately in the manner previously described.

The deposits were satisfactory in appearance except those obtained

from the solution in which the nickel sulphate content was only 35 grams per litre. These particular deposits Y<sub>1</sub> and N<sub>1</sub> were slightly "burnt," i.e., contained co-deposited hydroxide or basic salts of nickel the concentration of nickel ions having been too low for the current density used, so that the results of the hardness tests on these deposits are not significant and are only included as a matter of interest. The results are shown in Table VI.

TABLE VI.—HARDNESS AND STRESS IN NICKEL DEPOSITED FROM SOLUTIONS CONTAINING (1) AMMONIUM SULPHATE, (2) BORIC ACID.

*Depositing conditions.*—Temperature, 35° C. Cathode current density, 11 amps./sq. ft. Anode current density, 6 amps./sq. ft. Thickness of deposits, 0·01 in. Highly purified nickel anodes and solutions prepared from specially purified materials were used.

Reference Number.	Bath (see Table V.).	p <sub>H</sub> Range.	Cathode Efficiency.	Anode Efficiency.	Brinell Hardness Number 1 mm. Ball 10 kg. Load.	Stress (= Movement in mm. of One Strip for 0·005 in. Nickel Deposited).
18	Y <sub>1</sub>	5·8-6·5	94·06	—	281	—
4	Y <sub>2</sub>	5·5-6·15	98·0	99·82	293	1·65
12	Y <sub>2</sub>	5·5-6·2	98·47	100·1	289	1·21
23	Y <sub>2</sub>	5·9-6·3	98·37	—	297	1·10
27	Y <sub>3</sub>	5·8-6·5	98·24	—	278	—
8	Y <sub>4</sub>	5·5-6·15	97·97	98·22	315	1·16
16	Y <sub>4</sub>	5·5-6·05	—	—	292	1·38
24	Y <sub>4</sub>	5·9-6·05	99·04	—	291	—
Average (excluding Y <sub>1</sub> ) . . .			98·35	99·38	294	1·30
17	N <sub>1</sub>	5·8-6·5	94·71	—	225	1·58
19	N <sub>2</sub>	5·75-6·0	98·0	—	171	1·63
20	N <sub>2</sub>	5·6-5·9	98·58	—	157	1·54
29	N <sub>3</sub>	5·65-6·0	97·59	—	160	—
2	N <sub>4</sub>	5·5-5·7	—	100·1	161	1·82
7	N <sub>5</sub>	5·65-6·0	98·63	100·0	171	1·66
21	N <sub>5</sub>	5·7-5·8	99·13	—	155	1·83
22	N <sub>5</sub>	5·7-5·9	99·22	—	156	—
Average (excluding N <sub>1</sub> ) . . .			98·52	100·0	162	1·68

The results shown in Table VI. indicate that a pronounced difference in hardness exists between deposits produced from the solution containing boric acid on the one hand and ammonium sulphate on the other, when specially purified solutions and anodes are used, as well as with solutions and anodes of commercial purity as shown previously (see Table III.).

The hardness of deposits obtained in the N type of bath containing boric acid was not appreciably affected by large changes in the nickel content of the solution (*viz.*, 70 to 240 grams nickel sulphate NiSO<sub>4</sub> · 7H<sub>2</sub>O per litre) and similarly a change in nickel content of the Y type of solution containing ammonium sulphate from 70 to 120 grams nickel sulphate NiSO<sub>4</sub> · 7H<sub>2</sub>O per litre, does not cause any marked difference in the hardness of the deposit.

It can be seen, by a comparison of the hardness figures for deposits produced in baths Y<sub>2</sub>, Y<sub>3</sub>, N<sub>2</sub> and N<sub>3</sub> that variations in the potassium chloride content of the solution from 8 to 19 grams potassium chloride per litre does not result in any appreciable change in hardness.

The evidence thus obtained under conditions which almost entirely exclude the presence of impurities indicates that the difference in hardness of deposits produced from the two types of solution lies solely in the presence of boric acid in the one and of ammonium sulphate in the other.

The results of the stress measurements indicate that no apparent connection exists between hardness and stress as the stress is of the same order of magnitude in both the hard and soft deposits.

Fig. 3 shows the structure typical of the deposits produced from the baths containing boric acid. Large elongated crystals can be seen disposed in a direction normal to the cathode surface. The deposits obtained in solutions containing ammonium sulphate had a very fine grained structure. Fig. 4 shows the microstructure of deposit No. 4 produced in solution Y<sub>2</sub>.

## 7. The Effect of Additions of Sodium Fluoride, Sodium Sulphate, etc.

It has been recommended by Blum<sup>5</sup> that in order to obtain hard deposits, nickel sulphate-boric acid solutions should be used, to which an alkaline fluoride or hydrofluoric acid is added. Thomas and Blum<sup>6</sup> state that a large addition of sodium sulphate to a nickel sulphate-boric acid solution increases the hardness of the deposits. Owing to the fact that in former case the deduction as to increase in hardness produced was based upon the tensile strength of the deposits and in the latter case was based the upon scratch hardness tests, it is not possible to compare the results directly with those obtained by the Brinell Hardness Test. It is also possible that the results were influenced by the presence of impurities.

In order to obtain a satisfactory comparison with the data shown in Table VI., deposits were prepared from solutions of similar composition to those used by Blum and Thomas. Salts and anodes of high purity were used and the experiments were carried out in the manner previously described.

The composition of the solutions are shown in Table V. and the results of hardness and stress tests are shown in Table VII.

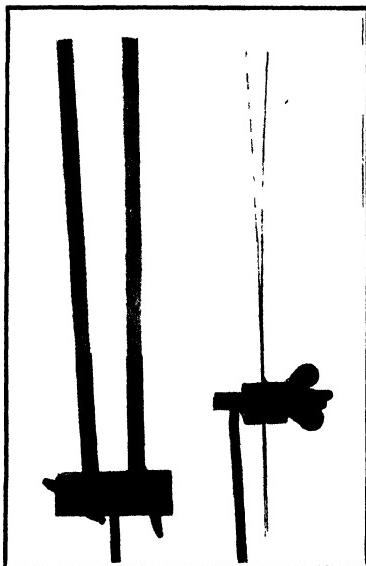
TABLE VII.—HARDNESS AND STRESS IN NICKEL DEPOSITED FROM SOLUTIONS CONTAINING (1) SODIUM FLUORIDE, (2) SODIUM SULPHATE.

*Depositing conditions.*—Temperature 35° C. Cathode current density, 11 amps./sq. ft. Anode current density, N<sub>7</sub> and 8·6 amps./sq. ft. Anode current density, N<sub>6</sub> and Y<sub>5·3</sub> amps./sq. ft. Thickness of deposits, 0·05 in. Highly purified nickel anodes and solutions prepared from specially purified materials were used.

Reference Number.	Bath (see Table V.).	p <sub>H</sub> Range.	Cathode Efficiency.	Anode Efficiency.	Brinell Hardness Number 1 mm. Ball 10 kg. Load.	Stress (= Movement in mm. of One Strip for 0·05 in. Nickel Deposited).
10	Y <sub>5</sub>	5·8-6·25	96·40	99·22	292	1·67
28	Y <sub>5</sub>	5·65-6·15	98·28	—	318	1·52
—	—	—	—	—	—	1·85
11	N <sub>6</sub>	5·4-3·5	94·58	88·22	250	1·69
25	N <sub>6</sub>	6·0-4·9	93·46	—	249	1·73
26	N <sub>7</sub>	5·65-6·3	95·6	—	232	2·52
13	N <sub>8</sub>	5·7-6·0	98·56	100·1	222	2·98

<sup>5</sup> Use of Fluorides in Solutions for Nickel Deposition." W. Blum, *Trans. Amer. Electrochem. Soc.*, 1921, **39**, 472.

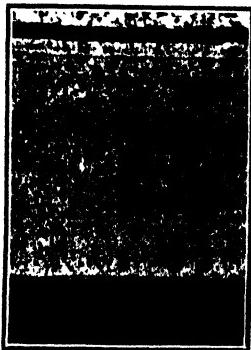
<sup>6</sup> "Protective Value of Nickel Plating." C. T. Thomas and W. Blum, *Trans. Amer. Electrochem. Soc.*, 1925, **48**, 84.



A                    B  
FIG. 1.



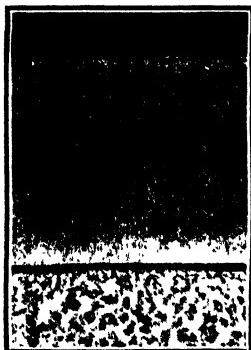
Bath N2. Brinell Hardness No. 171.  
FIG. 3. ( $\times 100$ ).



Bath Y2. Brinell Hardness No. 293.  
FIG. 4. ( $\times 100$ ).



Bath N8. Brinell Hardness No. 222.  
FIG. 5. ( $\times 100$ ).



Bath N6. Brinell Hardness No. 250.  
FIG. 6. ( $\times 100$ ).

[To face page 396.]



The results show that an increase in hardness is produced by the addition of a large amount of sodium sulphate or the substitution for potassium chloride of an equivalent amount of sodium fluoride in nickel sulphate solutions containing boric acid. The microstructures of the deposits shown in Figs. 5 and 6 show a decrease in the grain size of the deposits corresponding to the increase in hardness.

In neither case, however, is the hardness of these deposits (N6 N7 N8 Table VII.) as high as that of the deposits obtained in the nickel sulphate solutions containing ammonium sulphate (Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub>, Y<sub>4</sub> Table VI.) nor is the hardness of deposits from the latter type of solution appreciably affected by the substitution of sodium fluoride for potassium chloride Y<sub>5</sub> Table VII.

A serious drawback to the use of the solutions containing fluorides is the low anode and cathode efficiency. A disadvantage of the solutions containing sodium sulphate is the high stress in the deposit.

### **8. The Value of Ammonium Sulphate as an Addition to Nickel Sulphate Solutions.**

Ammonium sulphate until recently was extensively used as an addition to nickel sulphate solutions, its advantages being considered to be due to (1) the increased conductivity it secured, and (2) its effect in preventing the separation of basic nickel compounds at the cathode such as occurs when nickel is deposited from a solution containing nickel sulphate alone. A disadvantage of its use, however, lies in the low solubility of nickel ammonium sulphate which limits the concentration of nickel sulphate that can be used in the solution. A low nickel content in the solution places a restriction upon the current density which can be employed, and this may be a serious drawback where high rates of deposition are desired. As a consequence there has been an increased use of solutions from which ammonium sulphate is excluded, the most frequently used solutions being those containing nickel sulphate boric acid and potassium chloride and having a nickel content within the range studied in this investigation.

The results of this investigation, however, while confirming the generally recognised value of boric acid as an ingredient in nickel sulphate solution for the production of relatively soft deposits, indicates the value of ammonium sulphate when relatively hard deposits are required.

It would thus appear probable that the use of ammonium sulphate as an addition agent to nickel depositing solutions will be continued where deposits of high hardness and high resistance to wear are particularly required. Examples of such uses are the production of nickel electrotypes and various engineering applications, as the building up and repair of worn or undersized parts.

For this reason the precise influence of ammonium sulphate and other ammonium salts upon nickel depositing solutions will continue to be of interest.

The particular aspects of this influence which require elucidation are (1) the manner in which the presence of the salt in nickel sulphate solutions prevents the precipitation of basic nickel compounds at the cathode, (2) the reason or reasons why its presence results in the production of nickel deposits of high hardness.

#### **Prevention of Precipitation of Basic Salts in Deposit.**

An indication of the value of ammonium sulphate in this respect is suggested by its marked buffer action in a nickel sulphate solution within

the range of  $p_H$  used for the electro-deposition of nickel. This is shown in Fig. 7 by a comparison of titration curves obtained for a nickel sulphate solution with and without additions of ammonium sulphate. The curve I shows that the addition of only 19.5 c.c. of  $N$  sodium hydroxide causes a change in  $p_H$  of from 6.15-7.35 in a solution of nickel sulphate, whereas about 68 c.c. of the alkali are required to produce a similar change in  $p_H$  in the solution of nickel sulphate containing ammonium sulphate (curve II).

That the buffer action of ammonium sulphate is pronounced, although inferior to that of boric acid, is shown by a comparison of titration curves II and III. Precipitation of basic salts of nickel, however, does not occur in

the solution containing ammonium sulphate until a  $p_H$  of 7.6 is reached as against a  $p_H$  of 6.6 when boric acid is used.

The buffering effect of ammonium sulphate during nickel deposition would appear to be as follows. In the cathode film during deposition from a nickel sulphate sol-

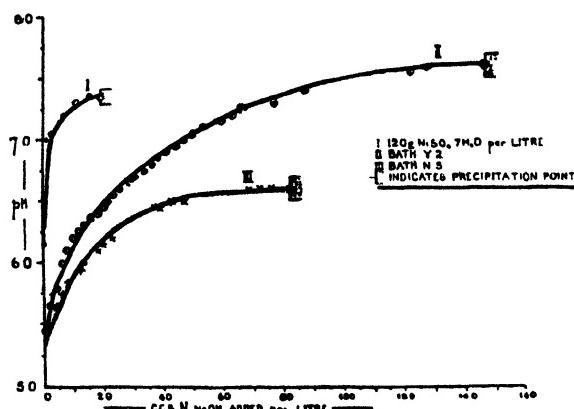


FIG. 7.—Comparative buffering : properties of nickel solutions.

hydrogen as well as nickel ions there is a tendency for such an increase in the concentration of hydroxyl ions to occur as to cause a precipitation of basic salts in the deposit. With the addition of ammonium sulphate to such a solution  $\text{NH}_4^+$  ions are present in the cathode film and these probably interact with hydroxyl ions to form slightly dissociated ammonium hydroxide and thus suppress the rate of increase of the hydroxyl ions, so that the  $p_H$  does not readily rise to such a value that precipitation of basic salts occurs. If this view is correct ammonium sulphate differs in its method of buffering the solution from that of boric acid since the latter would appear to function as a reservoir for the supply of fresh hydrogen ions to compensate for the loss which occurs at the cathode surface during deposition.

#### Production of Hard Deposits.

(a) *Influence of Ammonium Sulphate upon Nickel Ion Concentration.*—Reduction of the metal ion concentration of a depositing solution tends to increase the deposition cathode potential and this is generally assumed to cause a reduction in the average size of the crystals<sup>7</sup> and an increase in the hardness of the deposit.

As the addition of ammonium sulphate to a nickel sulphate solution produces an increase in the concentration of the common ion ( $\text{SO}_4^{2-}$ ) and in consequence causes a decrease in the nickel ion concentration, it is important to ascertain whether this effect is adequate to account for the high hardness of the deposits produced in the presence of this salt.

<sup>7</sup> "The Crystalline Form of Electrodeposited Metals." W. Blum and H. S. Rawdon, *Trans. Amer. Electrochem. Soc.*, 1923, 44, 397.

Cathode potential measurements were made at various current densities in solutions similar in composition to those previously described. The results are shown graphically in Fig. 8.

It appears that the cathode potential for a particular current density in a typical nickel sulphate ammonium sulphate solution which yields hard deposits is in general higher than the cathode potential for the same current density in a typical nickel sulphate boric acid solution which yields softer deposits. The difference in cathode potential is, however, not very considerable, and does not appear to be adequate to account for the very pronounced difference in hardness.

The relative insignificance of any relationship between deposition potential and the hardness of the corresponding nickel deposit is confirmed by a comparison of the cathode potential measurements in the above-mentioned solutions with those obtained in a solution of nickel sulphate and boric acid containing a high concentration of sodium sulphate shown in curve VI. In this solution the influence of the addition of a concentration of the common ion ( $\text{SO}_4^-$ ) greater than in the case of the nickel sulphate ammonium sulphate solution has caused a greater decrease in the nickel ion concentration and in consequence has caused a higher deposition cathode potential.

Yet the hardness of the deposits obtained was lower than of those obtained from the nickel sulphate ammonium sulphate solution.

(b) *Influence of Ammonium Sulphate upon Hydrogen Discharge.*—It has been assumed that another important factor which greatly influences the hardness of nickel deposits is the hydrogen which is discharged during nickel deposition and which may either modify the crystal structure by interfering with crystal growth or by the formation of a compound or alloy with the deposited metal.

Although differences in structure of deposits of nickel may finally be shown to be largely determined by the influence of hydrogen, the amount of hydrogen discharged does not appear to have been an important factor in influencing hardness figures given in this paper. The cathode efficiency measurements given in Table VI show that the amount of hydrogen discharged at the cathode in the solutions producing hard and soft deposits respectively was very similar.

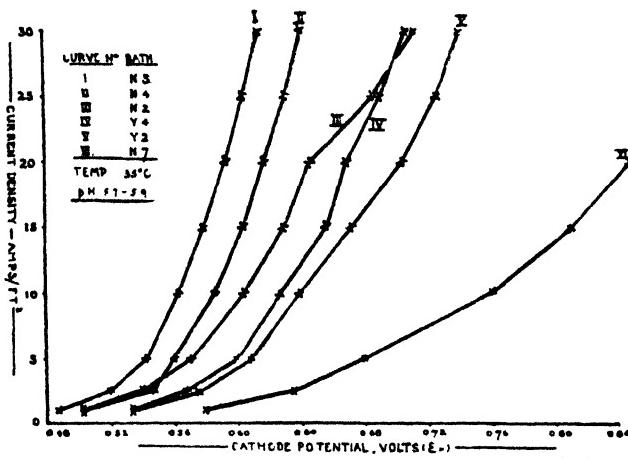


FIG. 8.—Cathode potential: current density curves in nickel solutions.

### Summary and Conclusions.

For the determination of the most suitable conditions for the electro-deposition of nickel for particular applications, methods for the quantitative determination of the hardness and relative stress in the deposits have proved of value. Various methods for the hardness testing of deposits are discussed, and it is concluded that the Brinell test is more accurate and reproducible than either the scratch hardness test or the scleroscope test. The minimum thickness of deposits of various hardnesses that can be tested accurately by the Brinell method with a 1 mm. ball and 10 kg. load have been calculated on the basis of Moore's results. An approximate method for rapidly ascertaining relative stresses in a nickel deposit is described.

The results of hardness tests and stress measurements in deposits obtained from a variety of nickel baths are given. The materials employed for the preparation of the solutions and the anodes used were specially refined and contained less than 0.01 per cent. impurity. The results show that hard deposits with a finely crystalline structure ranging in hardness from Brinell numbers 280-315 were obtained from solutions containing nickel sulphate, ammonium sulphate, and potassium chloride, while soft deposits of larger grain size ranging in hardness from Brinell numbers 155-170 were obtained from solutions containing nickel sulphate boric acid and potassium chloride.

The difference in hardness appeared to be entirely due to the presence of ammonium sulphate in the one solution and of boric acid in the other. The hardness results were independent both of the nickel sulphate concentration which was varied from 70 to 120 grams per litre and 70 to 240 grams per litre in the two types of solution respectively, and also of the potassium chloride which was varied from 8 to 19 grams per litre in each case. The tests were carried out at a temperature of 35° C., the highest temperature which could be safely used in practice where "stopping off" waxes were present.

It was found desirable to deposit at this temperature in view of the considerable reduction in stress which was obtained compared with a temperature of 20° C.

The Brinell Hardness of deposits obtained from solutions containing nickel sulphate boric acid and potassium chloride was found to be increased from an average of 162 to 250 and 227 respectively by large additions to the solution of sodium sulphate and by the replacement of the potassium chloride with an equivalent amount of sodium fluoride. The hardness of such deposits is not equal to that obtainable from baths containing ammonium sulphate and certain disadvantages attend the use of these baths. Thus the presence of fluorides in the solution results in low anode and cathode efficiencies, and solutions containing large amounts of sodium sulphate yield highly stressed deposits.

Possible reasons for the observed effect of ammonium sulphate in producing hard deposits are discussed.

# AN APPLICATION OF THE DONNAN THEORY TO THE ADSORPTION OF IONS BY COLLOIDAL SILICIC ACID.

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Received 12th March, 1928.

In this investigation an attempt is made to measure the adsorption of ions from hydrochloric acid by particles of colloidal silicic acid, using the Donnan theory for a semi-permeable membrane. The above theory has been used by Bjerrum<sup>1</sup> to measure the adsorption of ions by colloidal chromium hydroxide, whilst Rinde<sup>2</sup> has determined the adsorption in the case of colloidal sulphur. The applicability of the Donnan theory to such systems has been discussed by Bjerrum.<sup>1</sup>

An ion adsorbed by a colloid particle gets fixed on it, as it were, and may be treated as a non-dialysable ion. If a colloidal solution having a preferential adsorption for one of the ions of the electrolyte (hydrochloric acid), is put inside a semi-permeable membrane, the electrolyte being outside the membrane, then at equilibrium the following relation holds:—

$$\frac{a_{H_i}}{a_{H_o}} = \frac{a_{Cl_i}}{a_{Cl_o}}$$

where  $a_{H_i}$  and  $a_{H_o}$  are the activities of the hydrogen ions inside and outside the membrane,  $a_{Cl_i}$  and  $a_{Cl_o}$  being the corresponding quantities for chlorine ions. If the ions adsorbed are cations, then it can be shown<sup>2</sup> that

$$X_{\text{cation}} = \frac{a_{H_o}}{f} \left( \frac{a_{H_o}}{a_{H_i}} - \frac{a_{H_i}}{a_{H_o}} \right),$$

where  $X$  represents the amount of ion adsorbed, and  $f$  is the activity coefficient of the acid outside the membrane at equilibrium. Similarly, if the colloid adsorbs anions,

$$X_{\text{anion}} = \frac{a_{H_o}}{f} \left( \frac{a_{H_i}}{a_{H_o}} - \frac{a_{H_o}}{a_{H_i}} \right).$$

From the above relation it is possible to calculate the amount of ions adsorbed by colloidal particles from solutions of hydrochloric acid, if, at equilibrium, the activities of hydrogen ions inside and outside the membrane as well as the activity coefficient of the acid in the outer solution are determined.

In the practical application, however, of the above principle one is limited in the choice both of the colloid and of the electrolyte. The colloid should be fairly incapable of diffusion through the membrane, and keep stable in contact with the solution of the electrolyte used—a condition satisfied by few colloidal solutions. Colloidal silicic acid which is known to be quite stable in contact with hydrochloric acid, and to adsorb ions from it, has been used in the present investigation.

Colloidal solutions of silicic acid were prepared by Graham's method, by the hydrolysis of methyl silicate,<sup>3</sup> by the hydrolysis of silicon tetrachloride,<sup>4</sup>

\* Communicated by Professor F. G. Donnan.

<sup>1</sup> Z. physik. Chem., 110, 656, 1924.

<sup>2</sup> Phil. Mag., 1 (VII.), 32, 1926.

<sup>3</sup> Grimaux, Compt. rend., 98, 1434; 1884.

<sup>4</sup> Ebler and Fellner, Ber., 44, 1915, 1911.

and also by the hydrolysis of silicon disulphide.<sup>5</sup> The permeability of Graham's silicic acid has been studied by Zsigmondy and co-workers and more recently by Brintzinger.<sup>6</sup> Their investigations show that Graham's silicic acid is highly diffusible, and that under certain conditions of dialysis so much as 90 per cent. of the colloid passes through a collodion membrane, which is fine enough to stop completely the passage of a colloidal solution of silver.<sup>7</sup> Graham's silicic acid could not be used in the present investigation for the above reason. The diffusibilities of the colloid obtained from methyl silicate and of that from silicon tetrachloride, were investigated in a preliminary series of experiments. The membrane used was obtained from a 6 per cent. solution of collodion. The results are given in Tables I. and II. :—

TABLE I.—DIFFUSIBILITY OF COLLOIDAL SILICIC ACID PREPARED FROM METHYL SILICATE AGAINST HYDROCHLORIC ACID.

Strength of HCl outside.	Strength of Sol inside the Collodion Bag.	Strength of Sol outside the Bag.	Percentage of Sol passing through.
2·25 N	0·70 per cent.	0·009 per cent.	1·28
0·33 N	0·70 "	0·007 "	1·00
0·13 N	0·70 "	0·005 "	0·71
0·10 N	0·70 "	0·005 "	0·71

TABLE II.—DIFFUSIBILITY OF COLLOIDAL SILICIC ACID PREPARED FROM SILICON TETRACHLORIDE AGAINST HYDROCHLORIC ACID.

Strength of HCl outside.	Strength of Sol inside the Collodion Bag.	Strength of Sol outside the Bag.	Percentage of Sol passing through.
2·00 N	0·30 per cent.	0·026 per cent.	8·70
1·00 N	0·30 "	0·024 "	8·00
0·50 N	0·18 "	0·012 "	6·67
0·08 N	0·20 "	0·012 "	6·00
0·06 N	0·20 "	0·010 "	5·00

It is seen from Tables I. and II. that the diffusibility of the colloid obtained from methyl silicate is small as compared with that obtained from silicon tetrachloride. While the diffusibility of the colloid does not change in any regular manner with the strength of the acid outside the membrane, the general conclusion that diffusibility increases with increase of the strength of acid used, seems to be justified from the results obtained. The diffusibility of the colloid obtained from methyl silicate decreases with increasing dilutions of acid, and may be neglected at dilutions greater than 0·1 N.

The colloid obtained from the hydrolysis of silicon sulphide, apart from the difficulty of preparing the pure sulphide, was found to contain adsorbed hydrogen sulphide, which would vitiate subsequent adsorption measurements. This colloid was therefore not used in this investigation.

The collodion bag was prepared from a six per cent. solution of collodion; 30 c.c. of the colloid were put into the bag, which was then set up for dialysis, the outer vessel containing hydrochloric acid of the required strength. It was necessary to protect the inner and outer solutions from atmospheric carbon dioxide. Small equal volumes of the inner and outer

<sup>5</sup> Fremy, *Ann. Chim. Physique.*, [iii], 38, 312, 1853.

<sup>6</sup> Z. *anorg. Chem.*, 159, 256, 1927.

<sup>7</sup> Cf. Zsigmondy and Heyer, Z. *anorg. Chem.*, 68, 169, 1910.

solutions were drawn from time to time and their  $p_H$  measured. The attainment of equilibrium was tested by constancy in the value of the  $p_H$  of each solution. After equilibrium was reached, with each pair of inner and outer solutions measurements were made with the following cells:—

(1)  $H_2 | \text{Inner solution} || \text{Saturated KCl solution} || N\text{-calomel cell}$   
 $E = E_i$

(2)  $H_2 | \text{Outer solution} || \text{Saturated KCl solution} || N\text{-calomel cell}$   
 $E = E_o$

(3)  $H_2 | \text{Inner solution} || \text{Saturated KCl solution} || \text{Outer solution} | H_2$

$$E = E_m = \frac{RT}{F} \ln \frac{a_{H_i}}{a_{H_o}}$$

The platinum-hydrogen electrodes used in the above cells gave reproducible values for the *E.M.F.*. The value of the membrane potential  $E_m$  obtained directly checked well with the difference between  $E_i$  and  $E_o$ . The experimental results are assembled in Tables III. and IV. The values of  $a_{H_i}$  and  $a_{H_o}$  are calculated from the *E.M.F.* of cells (1) and (2), using the relation,

$$E - 0.2820 = \frac{RT}{F} \log \frac{1}{a_H}$$

The values for  $f$ , the activity coefficient of the acid in the outer compartment, are taken from the Table on p. 336, of "Thermodynamics" by Lewis and Randall.  $X$ , the amount of ions adsorbed by the colloid is calculated from the relation,

$$X_{\text{cation}} = \frac{a_{H_o}}{f} \left( \frac{a_{H_o}}{a_{H_i}} - \frac{a_{H_i}}{a_{H_o}} \right).$$

The last column in Tables III. and IV. gives the amount of ions adsorbed per unit weight of the colloid.

TABLE III.—(COLLOID OBTAINED FROM METHYL SILICATE.)

$E_i$ .	$E_o$ .	$a_{H_i}$ .	$a_{H_o}$ .	$f$ .	$X$ .	$\frac{X}{C}$
0.3924	0.3900	$1.34 \times 10^{-2}$	$1.480 \times 10^{-2}$	0.89	$3.161 \times 10^{-3}$	$5.270 \times 10^{-4}$
0.3740	0.3660	$2.76 \times 10^{-2}$	$3.776 \times 10^{-2}$	0.87	$2.797 \times 10^{-3}$	$3.999 \times 10^{-3}$
0.3702	0.3640	$3.199 \times 10^{-2}$	$4.070 \times 10^{-2}$	0.86	$2.301 \times 10^{-3}$	$4.425 \times 10^{-3}$
0.3460	0.3410	$8.22 \times 10^{-2}$	$1.000 \times 10^{-1}$	0.80	$4.932 \times 10^{-3}$	$5.032 \times 10^{-3}$
0.3270	0.3230	$1.728 \times 10^{-1}$	$2.018 \times 10^{-1}$	0.775	$8.128 \times 10^{-3}$	$1.211 \times 10^{-2}$
0.3246	0.3174	$1.897 \times 10^{-1}$	$2.513 \times 10^{-1}$	0.770	$1.850 \times 10^{-1}$	$1.968 \times 10^{-2}$
0.3200	0.3122	$2.27 \times 10^{-1}$	$3.078 \times 10^{-1}$	0.76	$2.504 \times 10^{-1}$	$2.153 \times 10^{-2}$
0.3074	0.3115	$3.712 \times 10^{-1}$	$3.163 \times 10^{-1}$	0.76	$1.339 \times 10^{-1}$	$2.231 \times 10^{-2}$

TABLE IV.—(COLLOID OBTAINED FROM SILICON TETRACHLORIDE.)

$E_i$ .	$E_o$ .	$a_{H_i}$ .	$a_{H_o}$ .	$f$ .	$X$ .	$\frac{X}{C}$
0.3710	0.3820	$3.097 \times 10^{-2}$	$2.023 \times 10^{-2}$	0.88	$2.018 \times 10^{-2}$	$1.009 \times 10^{-3}$
0.3469	0.3575	$7.943 \times 10^{-2}$	$5.260 \times 10^{-2}$	0.85	$5.246 \times 10^{-2}$	$2.623 \times 10^{-2}$
0.3450	0.3540	$8.551 \times 10^{-2}$	$6.026 \times 10^{-2}$	0.83	$5.187 \times 10^{-2}$	$2.593 \times 10^{-2}$
0.3280	0.3320	$1.662 \times 10^{-1}$	$1.421 \times 10^{-1}$	0.79	$5.732 \times 10^{-2}$	$2.866 \times 10^{-2}$
0.3220	0.3250	$2.099 \times 10^{-1}$	$1.867 \times 10^{-1}$	0.78	$5.018 \times 10^{-2}$	$3.121 \times 10^{-2}$
0.3166	0.3190	$2.654 \times 10^{-1}$	$2.360 \times 10^{-1}$	0.77	$7.211 \times 10^{-2}$	$4.005 \times 10^{-2}$
0.3093	0.3120	$3.444 \times 10^{-1}$	$3.101 \times 10^{-1}$	0.76	$8.576 \times 10^{-2}$	$4.288 \times 10^{-2}$
0.2840	0.2860	$9.249 \times 10^{-1}$	$8.555 \times 10^{-1}$	0.82	$1.029 \times 10^{-1}$	$8.145 \times 10^{-2}$

### Discussion of Results.

In Figs. 1 and 2,  $\alpha_{H_0}$  the activity of H-ion in the outer solution is plotted against  $\frac{X}{C}$ , the amount of ions adsorbed per unit weight of the colloid. It

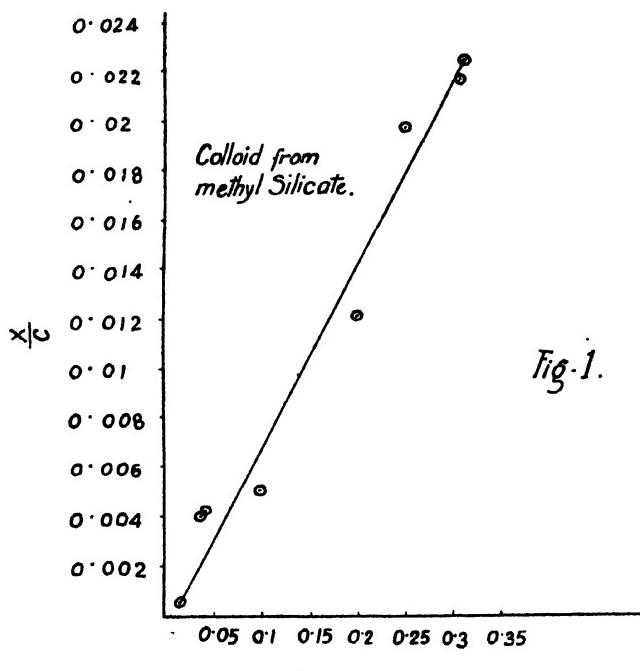


Fig. I.

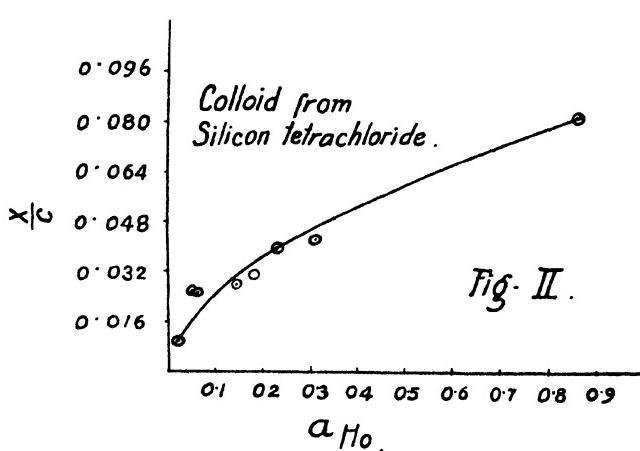


Fig. II.

is evident from Tables III. and IV., that the colloid obtained from methyl silicate adsorbs hydrogen ions, while that obtained from silicon tetrachloride adsorbs chlorine ions, even when the concentration of the acid used in both cases is the same. In the former case the amount of hydrogen ions adsorbed is found to be a linear function of the activity of the acid in the outer vessel (see Fig. 1). With the colloid from silicon tetrachloride, the adsorption-activity curve takes the form of the usual Freundlich isotherm (Fig. 2).

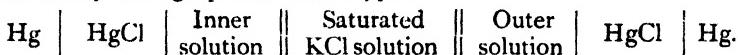
The nature of the ion adsorbed seems to depend on the activity of the acid used, as will be seen from Table III.

Up to a value

of  $\alpha_{H_0} = 3.078 \times 10^{-1}$ , the colloid adsorbs hydrogen ions, while for  $\alpha_{H_0} = 3.163 \times 10^{-1}$ , chlorine ions are adsorbed in preference to hydrogen ions. It is interesting to note in this connection that in neutral, alkaline or weakly acid solutions silicic acid hydrosols are negatively charged, whereas in the presence of stronger acids the sign of the charge is reversed,

the colloid becoming positively charged.<sup>8</sup> There seems, however, to be no definite relation between the sign of the charge on the colloid particle and the nature of the ion which is adsorbed preferentially. Rinde<sup>2</sup> has shown that negatively charged colloidal sulphur adsorbs chlorine ions while Bjerrum has found that positively charged chromium hydroxide also adsorbs chlorine ions. The highly amphoteric nature of silicic acid and the charge reversal brought about by variation in the strength of acid used, run parallel with the peculiarity of the adsorption phenomena already referred to.

That the colloid obtained from silicon tetrachloride adsorbs chlorine ions even from solutions of hydrochloric acid of low concentrations was confirmed by setting up cells of the type :—



Measurements of the activity of chlorine ions from the above cell agreed fairly well with the values calculated from the measurements of hydrogen ion activities from cells already described.

Silicic acid is also likely to adsorb molecules of hydrochloric acid, but no attempt is made to estimate the quantity so adsorbed. In this investigation a measurement is obtained only of the amount of an ion adsorbed in preference to the other ion of the binary electrolyte.

From these measurements the conclusion seems to be justified that colloidal silicic acid prepared from silicon tetrachloride has a preferential adsorption for chlorine ions, whilst the colloid from methyl silicate adsorbs hydrogen ions preferentially. This difference in behaviour towards the nature of ions adsorbed is probably connected with the method of preparation of the colloid.

### Summary.

1. Adsorption of ions from hydrochloric acid by particles of colloidal silicic acid prepared by different methods, has been measured by the application of the Donnan membrane equation.

2. Measurements were made of the diffusibility of the colloids through collodion membrane.

3. The amount of ion adsorbed was found generally to increase with the activity of the acid from which the ion is adsorbed.

The colloid prepared from silicon tetrachloride showed a preferential adsorption for chlorine ions, while that from methyl silicate had a preference for hydrogen ions.

<sup>8</sup> Cf. Billiter, *Z. physik. Chem.*, 51, 150, 1905.

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## THE VAPOUR PRESSURES OF BINARY SYSTEMS.

By ALFRED W. PORTER, D.Sc., F.R.S.

### PART II. GOLD AND MERCURY.

(Received 19th May, 1928.)

This paper is a continuation of one published in the June Transactions of the Society (p. 343). The systems now dealt with are those of gold and mercury.

The experimental determinations made use of are those of Eastman and Hildebrand.<sup>1</sup> The vapour pressures given are those corresponding to a temperature of about 316° C. At that temperature gold is soluble to the extent of about one-seventh molar fraction. The molar fractions at any concentration are  $\mu_1$  for mercury and  $\mu_2$  for the gold. The data are as follows: the symbol  $a_1$  denoting the ratio of the vapour pressure of mercury for the solution to that for pure mercury:—

$\mu_2.$	$a_1.$	$\mu_2.$	$a_1.$
.0152	.987	.1046	.945
.0398	.979	.1179	.942
.0652	.968	.153	.931
.0717	.955	.191	.933
.0925	.950		

An expression  $\log (a_1/\mu_1) = \frac{\beta\mu_2^2}{(1 + \rho\mu_2)^2}$  has been hitherto fitted to these values. This equation, however, is of a form forbidden by Margules' equation, and it fails to bring out important properties of the mixture. The following equation is of a permissible form:—

$$\log a_1 = \alpha \log \mu_1 + \beta \mu_2^2 + \gamma \mu_2^3 (4 - 3\mu_2),$$

and it satisfies the experimental data if

$$\alpha = .91, \quad \beta = 1.998, \quad \gamma = - .78,$$

if logarithms to base ten are employed. If natural logarithms are preferred,  $\alpha$  remains unchanged, but  $\beta$  and  $\gamma$  must be multiplied by 2.3026.

The experimental data are shown as circles on Fig. 1. This figure is

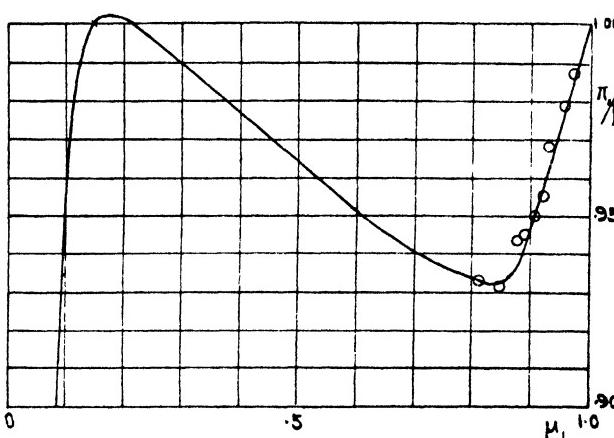


FIG. 1.—Gold in mercury.

was shown in the previous paper that when the curve ascends from right to left the system is unstable; any fortuitous evaporation there encouraging still more evaporation. One experimental point lies in this region and corresponds to a supersaturated state. It lies on the calculated curve. The saturation point is thus discovered as the point at which the "forces" involved become an unstable system.

(2) By Margules' equation, the value of  $\alpha$  for the second component ( $\alpha_2$ ) is the same function of  $\mu_2$  that  $a_1$  is of  $\mu_1$ . The plotted curve is there-

on an open scale, the whole range of  $a_1$  being less than 0.1. The above curve, calculated for the whole range of values of  $\mu_1$ , is drawn as a continuous line. It has the following properties:—

(1) At the saturation point of the solution it turns rapidly round so that  $a_1$  increases with decreasing  $\mu_1$ . It

<sup>1</sup> J. Amer. Chem. Soc., 36, 2020, 1914.

fore also  $a_2$  against  $\mu_2$ . Now at the saturation point the solution is in equilibrium with the solute, and these two must have the same value of  $a_2$ . The diagram shows that  $a_2$  has the value unity when  $\mu_2$  is about 15. Thus the curve appears to be valid near both ends. The left-hand side represents the region of absorption for which the gold is in excess. This is a stable region.

(3) This equation should also give an approximate equation to the osmotic pressure even for concentrated solutions. For, provided the total hydrostatic pressure to which the solution is subjected is small,

$$Pu = - RT \log a_1,$$

where  $P$  is the osmotic pressure and  $u$  is the molecular volume of pure mercury. That is

$$P = - \frac{RT}{u} \{ .91 \log \mu_1 + 1.998 \mu_2^2 - \text{etc.} \} 2.3025.$$

Further, since  $\frac{d \log a_1}{d \mu_1}$  is zero for a saturated solution, it follows that such a solution is one for which the osmotic pressure ceases to change with change in the value of  $\mu_1$ .

### PART III. CALCIUM CHLORIDE AND WATER.

(Received 31st May, 1928.)

In this part aqueous solutions of calcium chloride will be considered at two temperatures in order to bring out the influence of temperature.

The data employed are the vapour pressures of water (in equilibrium with the solutions) obtained by Harrison and Perman.<sup>1</sup>

The values of  $a_1 = \pi_1/\Pi_1$  calculated from them are given below:—

At 80°.		At 40°.		At 40°.	
$\mu_1$ .	$a_1$ .	$\mu_1$ .	$a_1$ .	$\mu_1$ .	$a_1$ .
.9901	.974	.9942	.996	.9416	.728
.9772	.940	.9885	.989	.9267	.629
.9649	.889	.9823	.946	.9078	.504
.9509	.809	.9772	.942	.8841	.375
.9310	.678	.9729	.913	.8560	.252
.8995	.480	.9695	.900	.8752	.608
.8621	.317	.9632	.873		
.8213	.213	.9598	.842		
.8006	.178	.9535	.824		

The last given concentration is definitely a case of supersaturation. Saturation occurs at  $\mu_2 = 16$  about, for  $t = 40^\circ \text{ C.}$

It is found to be impossible to fit the experimental values except by employing four terms. The equations obtained are:—

For 80° C.

$\log_a a_1 = 2 \log_a \mu_1 - 35.4 \mu_2^2 - 110 \mu_2^3 (1 + 3\mu_1) + 185 \mu_2^4 (1 + 4\mu_1 + 10\mu_1^2);$   
and for 40° C.

$\log_a a_1 = \log_a \mu_1 - 37.7 \mu_2^2 - 304 \mu_2^3 (1 + 3\mu_1) + 576 \mu_2^4 (1 + 4\mu_1 + 10\mu_1^2).$

<sup>1</sup> Trans. Farad. Soc., 23, 1 (1927).

The coefficients of the various terms are

	$\alpha.$	$\beta.$	$\gamma.$	$\xi_1.$
At 80°	2	- 35.4	- 110	+ 185
At 40°	1	- 37.7	- 304	+ 576

The curves corresponding to these equations are shown by continuous lines on the figure. The experimental values are indicated by circles or black dots. Saturation occurs where the curves become horizontal. To the left of these points the mixture would be unstable.

The difference in  $\alpha$  is the most unexpected result; but it is indubitably given by the experimental results. The other terms on the right all vanish when  $\mu_2$  is zero and are of not less than the second order of small quantities when  $\mu_2$  is itself of the first order. The curves start from the top right-hand corner at different slopes and this requires the different values of  $\alpha$ . If Raoult's law were true for the molecules of solute reckoned as normal

molecules the dotted curve would be followed. This is very nearly indeed the case for the beginning of the 40° C. curve; but it is not so for 80° C. Hence the difference in  $\alpha$ . The value of  $\beta$  slightly falls with rise in temperature; it is nearly in inverse ratio to the absolute temperature. The values of  $\gamma$  and  $\xi_1$  both diminish fast with rise in temperature; they can be represented approximately by taking them

of the form  $e^{\frac{K}{T}}$  or  $e^{\frac{K'}{RT}}$ ; in the latter form, if  $R$  is the gas constant,  $K'$  is an energy term.

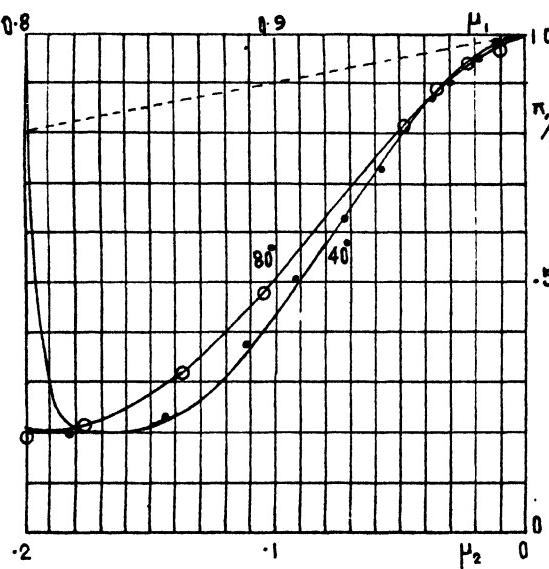


FIG. 2.—CaCl₂ at 80° C. and 40° C.

Similarly if  $\beta$  is written  $\frac{\beta_1}{RT}$  then  $\beta_1$  is also an energy term and is a measure of its contribution to the heat of dilution as is seen by introducing Kirchhoff's equation. It is necessary, however, to accumulate more data from which the variation of the coefficients with temperature can be more certainly determined before deducing the heat of dilution.

In determining the coefficients from the experimental values use has been made of the condition that when the solution is saturated the vapour pressure curve must be horizontal. This means that at this point

$$2\beta\mu_1\mu_2 + 12\gamma\mu_1^2\mu_2^2 + 60\xi_1\mu_1^3\mu_2^3 = \alpha.$$

Hence if from any other phenomena (such as heats of dilution) the coefficients were known at various temperatures it would be possible to determine the value of  $\mu_1\mu_2$  for saturation. Since at least four terms are necessary in the case of a substance like CaCl₂ it is not surprising that so little success has been obtained in the past in obtaining formulæ for saturation.

## COPPER HYDROSOLS OF LOW ELECTRICAL CONDUCTIVITY.

By G. T. R. EVANS.

Received 26th March, 1928.

The electrical conductivity of water solutions of colloidal copper prepared by the author seems to be lower than that of similar colloidal solutions previously published. In a paper on "The Coagulation of Colloidal Copper,"<sup>1</sup> Paine mentions with reference to his solutions that "the conductivity varied from  $1 \times 10^{-6}$  to  $3 \times 10^{-6}$  reciprocal ohms per centimetre cube." The lower limit actually reached (unpublished) was  $0.82 \times 10^{-6}$ . The lower limit of the range stated does not appear to have been extended by other workers. Previously Whitney and Blake<sup>2</sup> had prepared colloidal gold of conductivity  $1.8 \times 10^{-6}$  ohm<sup>-1</sup> cm.<sup>-1</sup>, and colloidal platinum of conductivity  $2.9 \times 10^{-6}$  ohm<sup>-1</sup> cm.<sup>-1</sup>, while Burton had prepared colloidal gold<sup>3</sup> of conductivity  $3.6 \times 10^{-6}$  ohm<sup>-1</sup> cm.<sup>-1</sup> and colloidal copper<sup>4</sup> of conductivity  $3.1 \times 10^{-6}$  ohm<sup>-1</sup> cm.<sup>-1</sup> at 18° C. Lately, Pauli<sup>5</sup> has prepared gold solutions of conductivity  $3 \times 10^{-6}$  ohm<sup>-1</sup> cm.<sup>-1</sup>.

The main object of this paper is to record the production, consistent over a period of eighteen months, of copper solutions, of conductivity a good deal below  $1 \times 10^{-6}$  ohm<sup>-1</sup> cm.<sup>-1</sup> at 20° C.

### The Method of Preparation.

The method of preparation of the copper solutions was based upon Bredig's process of pulverisation by the electric current using a copper arc in conductivity water.

Ordinary tap water was distilled in a copper still and then redistilled in a block tin still of about five litres capacity, after the addition of two or three small crystals of potassium dichromate and about six drops of concentrated sulphuric acid. The arrangement of the tin still was similar to that of the Jena glass still already described by Paine and Evans.<sup>6</sup> The first litre of the new distillate was thrown away and the next two or three litres of water were collected and kept in Jena glass litre flasks. These flasks with long necks were fitted with ground glass stoppers protected from dust with tall glass covers. The conductivity of the water thus obtained was measured, and if found to be above  $1 \times 10^{-6}$  ohm<sup>-1</sup> cm.<sup>-1</sup> was discarded. Only water of conductivity below  $1 \times 10^{-6}$  ohm<sup>-1</sup> cm.<sup>-1</sup> was used for the preparation of the copper solutions.

The arrangement of the apparatus for preparing the colloidal solutions was as shown in the figure.

<sup>1</sup> Proc. Camb. Phil. Soc., 16, 431 (1912).

<sup>2</sup> Phil. Mag. (6), 11, 436 (1906).

<sup>3</sup> Koll. Zeit., 38, 22 (1926).

<sup>4</sup> J. Am. Chem. Soc., 26, 1339 (1904).

<sup>5</sup> Ibid., (April, 1909).

<sup>6</sup> Proc. Camb. Phil. Soc., 18, 1 (1914).

The water was poured directly from its receiver into the short-necked flask A (of about 750 c.c.s capacity), which had been just previously rinsed with a portion of the same water. The flask A was then placed inside an empty cylindrical glass container B, and the whole raised into position so as to surround the copper electrodes C and D as indicated. Tap water was made to flow around A inside B so as to keep the former cool (about 20° C.). The overflow was taken away by the syphon.

The cathode D consisted of a copper rod, about 1 cm. diameter, and about 18 cm. long. It was clamped in a vertical position to a vertical steel spindle that was quickly rotated by the low voltage motor M. As the motor could only be used with its armature running about a horizontal axis, it was coupled to the vertical spindle by means of a bent spring drive. The anode C consisted of a piece of thin copper rod (S.W.G. 12) bent as shown

and held in place by a hinged clamp, the position of which was controlled by two adjustable helical springs stretching to the right and left. By altering the tensions in these springs with adjusting screws, the anode C could be made to touch the cathode D very lightly near its lower extremity, where "arcing" took place. It was found that for the maintenance of a suitable arc and the consequent preparation of a relatively high concentration of colloid, the true running of the rod D about its axis and a delicate adjust-

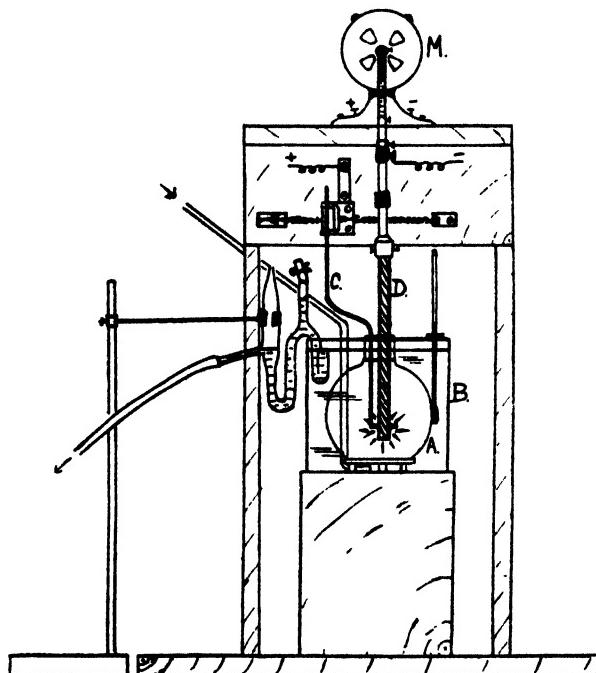


FIG. I.

ment of the rod C were essential.

In circuit with the electrodes were a battery of Edison cells of about 80 volts E.M.F., a regulating resistance and an ammeter. The current flowing across the arc was regulated to be from 8 to 10 amperes. Two hours was the time taken to prepare a sample of colloid. During the process a deep groove was eaten into the cathode where it made a running contact with the anode, but the anode itself, save for a roughened or blistered appearance, was practically unchanged. For the preparation of subsequent samples the anode had to be filed smooth and a new point of contact on the cathode chosen. When not in use the electrodes were allowed to stand in conductivity water which was protected from dust.

Immediately after its preparation the sample of colloid was put to stand for at least a day with the mouth of the flask protected by a glass cover.

During this time the larger particles of copper torn off in the discharge settled down and the colour of the solution changed from reddish-brown to very dark brown.

### Conductivity Measurements.

After the prepared sample of copper colloid had stood undisturbed for a day (or sometimes for several days), a portion of it was pipetted into a Jena glass conductivity cell, surrounded by a water bath at room temperature (about 20° C.). The Whetham double commutator method of measuring the resistance was adopted. From these readings the conductivity at 20° was deduced by applying the 2 per cent. per degree correction.

Table I. is a record of a number of copper colloid samples prepared. The concentration of each of the samples was determined by titrating with dilute nitric acid :—

TABLE I.

Copper Sample. Date.	Conductivity. $10^{-6} \omega^{-1} \text{ cm.}^{-1}$	Concentration. $10^{-6} \text{ gm. c.c.}^{-1}$	Conductivity of Water used. $10^{-6} \omega^{-1} \text{ cm.}^{-1}$
15/2/27	0.34	2.20	0.67
16/2/27	0.47	3.34	0.67
16/2/27	0.57	3.86	0.70
14/2/27	0.54	2.14	0.73
1/7/27	0.38	2.19	0.65
7/7/27	0.36	2.36	0.65
8/7/27	0.60	4.19	0.61
8/7/27	0.36	2.88	0.58
9/7/27	0.44	2.40	0.70
9/7/27	0.41	1.92	0.68
11/7/27	0.30	1.26	0.60
11/7/27	0.36	2.93	0.58
12/7/27	0.51	5.38	0.54
12/7/27	0.59	5.49	0.66
13/7/27	0.56	5.40	0.57
13/7/27	0.39	4.70	0.77

It may be pointed out that the low values of the conductivities are not due to relatively low concentrations. Table II. gives corresponding conductivities and concentrations of some "low conductivity" metallic colloids as recorded in the papers already referred to.

TABLE II.

Investigator.	Colloid.	Conductivity. $10^{-6} \omega^{-1} \text{ cm.}^{-1}$	Concentration. $10^{-4} \text{ gm. c.c.}^{-1}$
Whitney and Blake	Gold	$1.8 \times 10^{-6} \omega^{-1} \text{ cm.}^{-1}$	$1.46 \times 10^{-4} \text{ gm. c.c.}^{-1}$
Burton . . .	Gold	3.6	0.62
Burton . . .	Copper	3.1	0.88
Paine . . .	Copper	1.3	1.6
Pauli . . .	Gold	3.5	0.5

These show a much lower concentration than those of Table I.

Again, a comparison of the numbers in columns 2 and 4 of Table I. will show that in every case the initial conductivity of the water used in the

preparation of the colloid is not as low as that of the copper solution prepared from it. This may be due to the adsorption on the "copper" particles of impurities present in the water or to some chemical reaction in which ions are removed from solution. A similar effect had been previously observed by Nordlund ("Quecksilber-hydrosole," p. 86 (1918)) when preparing mercury hydrosols. Another point worth drawing attention to is that these solutions seemed to be very stable. When stored in Jena flasks for several weeks at any rate, they showed no signs of settling. The conductivity had certainly gone up after a few months, but whether this effect was due to solution of the glass or to some gradual change in the particles themselves was not determined.

Further investigations on the low conductivity copper hydrosols are being carried out in this laboratory.

In conclusion, I wish to thank Professor Paine for his kind assistance at all times.

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## CATAPHORESIS IN COPPER OXIDE SOLS. THE APPLICATION OF DEBYE AND HÜCKEL'S THEORY OF ELECTROLYTIC CONDUCTION TO COLLOID PARTICLES.

By H. H. PAYNE.

*Received 26th March, 1928.*

### Introduction.

The preparation in this Laboratory<sup>1</sup> of copper oxide sols (often termed simply copper sols) of extremely low conductivities, and therefore of very small electrolyte content, has made it appear worth while to measure afresh the velocities of the particles of such sols in an electric field. Hitherto, measurements of this velocity have yielded very divergent results, and it has generally been recognised that this divergence is due to the varying conductivities of the different sols examined. Thus Burton<sup>2</sup> with copper sols of conductivities varying from  $8.2 \times 10^{-6}$  to  $3.1 \times 10^{-6}$  found mobilities (at 18° C.) ranging from  $23.4 \times 10^{-6}$  to  $33.0 \times 10^{-6}$ —the lower the conductivity of the sol, the higher the mobility of the particles. These results suggest that further purification of the sol would yield still higher values for the velocity of the particles in an electric field.

This paper contains an account of these new mobility measurements in which the transportation method was employed. Experiments were also made with copper oxide sols to which varying amounts of electrolyte had been added, and though these experiments were not extensive, it seemed worth while to record them, because they throw some light on the modern theory of electrolytic conduction and cataphoresis as developed by Debye and Hückel, and on the relation between colloid particles and "true" ions.

<sup>1</sup> Evans, This Journal, p. 409.

<sup>2</sup> Phil. Mag., 17, 586, (1909).

Similar experiments of Freundlich and Zeh,<sup>3</sup> which are much more extensive and complete, yield similar results when examined in the same way.

### Method of Experiment.

For mobility measurements, use was made of the Hittorf transportation method, first extended to colloidal solutions by Duclaux. This method has not been employed very extensively, though judging from the recent experiments of Engel and Pauli<sup>4</sup> the results obtained by its use are probably more trustworthy than those deduced from observations on moving boundaries.

The form of apparatus adopted in the experiments to be described was a simplified form of Wintgren's arrangement.<sup>5</sup> An inverted U-tube, measuring about 28 cms. in length from one open end to the other and 1·3 cms. in diameter, dipped into two small 100 c.c. flasks placed side by side (Fig. 1). The electrodes consisted of two platinum strips, 1 cm. wide, wrapped round the tube about half a centimetre from the two ends. Platinum wires welded to these strips passed along the outside of the tube and were bound each to its own limb near the top, where also they were welded to copper wires for connecting to the source of E.M.F. The liquid was made to fill the tube by suction applied to a narrow tube fused to the top of the inverted U. At the end of the experiment this tube was opened and the liquid fell back into the two flasks. The contents of the two flasks were then analysed.

The velocity of the particles may be calculated as follows.<sup>6</sup> Consider any cross-section, area  $A$ , of the tube joining the anode vessel and the cathode vessel. Let  $F$  be the potential gradient in volts per centimetre at this cross-section,  $v$  the velocity of the particles when the potential gradient is one volt per centimetre (*i.e.* their mobility), and  $M$  the mass of colloid per cubic centimetre of the sol. Then the mass of colloid  $m$  crossing the given section in time  $t$  is  $FvAtM$ . This is the gain of colloid on the one side, and the loss on the other. We thus have the equation

$$v = \frac{m}{M} \cdot \frac{I}{FAt} \quad . . . . . \quad (1)$$

If  $k$  be the specific conductivity of the liquid (in reciprocal ohms "per centimetre cube") and  $i$  be the current flowing (in amperes), then  $i = FkA$ , so that equation 1 becomes

$$v = \frac{m}{M} \cdot \frac{k}{i} \cdot \frac{I}{t} \quad . . . . . \quad (2)$$

For any given cell for which the electrodes are fixed we have

$$k/i = p/V \quad . . . . . \quad (3)$$

<sup>3</sup> *Z. physik. Chem.*, 114, 65, (1924).

<sup>4</sup> *Ibid.*, 126, 247, (1927).

<sup>5</sup> *Ibid.*, 103, 238 (1922).

<sup>6</sup> Compare Grundmann, *Koll. Beihefte*, 18, 199 (1923), also Engel and Pauli, *loc. cit.*

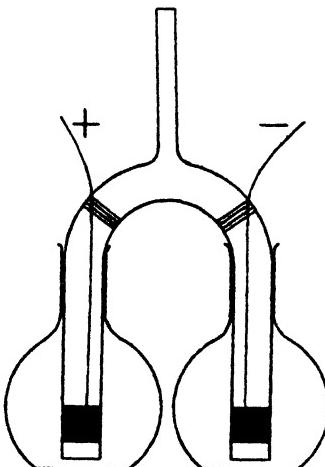


FIG. 1.

where  $V$  is the potential difference applied to the electrodes, and  $\rho$  is a constant which we may term the cell constant. Hence finally,

$$v = \frac{m}{M} \cdot \frac{\rho}{V} \cdot \frac{I}{t} \quad \dots \quad \dots \quad \dots \quad (4)$$

$\rho$  can be determined once for all by measuring the current through the cell when a solution of known conductivity is placed in it—making use of equation 3. ( $V$  might also be taken as the potential difference between any two fixed points in the connecting tube—measured by an electrometer, say.)

The transportation experiment, therefore, reduces itself to measuring the total colloid transported—lost on the one side, gained on the other—under the application of a known potential difference. No problem of the cross-section of the tube, or even of its uniformity, arises.

There are several features of this method of experiment and of the particular form of apparatus adopted which are worth mentioning. In the first place, the point in the tube at which the velocity of the particles is determined is at the top of the inverted U, where the colloid particles pass over from one side to the other. Here there can be no complications arising from boundary conditions, and the colloid particles under observation are certainly those in the body of the liquid. In the second place, this point in the electric circuit is midway between the two electrodes, and therefore electrolyte changes at these electrodes are *least* likely to affect the particles which are transported. Thirdly, the danger of contamination with impurities before and during the experiment is reduced to a minimum. Liquid in bulk is made use of—contrast experiments with the ultramicroscope. All taps with grease are avoided. Both flasks and tube can be cleaned thoroughly and easily, and no solid material other than glass and platinum comes near the liquid. Contamination from the air during the experiment is avoided, for the limbs of the tube very nearly close the necks of the flasks. The problem of avoiding contamination was of special importance in these experiments, since very pure colloidal solutions were being examined.

One drawback to such a transportation apparatus is that it does not lend itself to the use of a (constant temperature) water bath. In the following experiments the flasks and tube were placed on a narrow platform supported by a rod, and a large beaker brought up from below surrounded them. This beaker was simply covered with a sheet of cardboard through which the supporting rod, upper tube, and wire leads were brought. The thermometer which recorded the temperature (to one-tenth of a degree) was placed with its bulb near the transport tube.

It was assumed that the reading of this thermometer gave the temperature of the liquid in the tube with sufficient accuracy. There will always be a difference of temperature between the liquid and the air outside, however, if the temperature of the air is changing. The rate of such a change never exceeded half a degree C. per hour in any of the experiments recorded. In order to determine what sort of difference in temperature between the liquid and the air would result in such circumstances, a piece of glass tube exactly like that used for the transportation experiments was filled with warm water and its rate of cooling observed—a thermometer in the tube giving directly the temperature of the water. From these observations one was able to calculate directly what difference in temperature between the inside and the outside would change the temperature of the water at the rate of half a degree per hour. The result was approximately one-sixth of

a degree. An error of this amount in recording the temperature of the liquid will produce an error of less than one-half per cent. in the calculated velocity of the colloidal particles for some particular temperature. The above estimate of temperature difference was confirmed by direct observation of the two thermometers, one inside the tube and the other outside, for various rates of temperature change in the outside air.

Again, the heating effect of the current will tend to produce a difference of temperature between the liquid and the outside air. This effect was usually quite negligible, however. When the purest copper sol was in the tube, the current was in the neighbourhood of  $0.4 \times 10^{-5}$  amp. The potential gradient in the tube was about 8 volts per cm. Consequently the heat evolved per hour per centimetre was 0.028 cal. With other solutions, to which electrolyte had been added, the current was considerably greater, but only in one or two solutions was it greater than  $10^{-4}$  amp., in which case about 0.7 cal. would be evolved per centimeter during the hour. The volume of 1 cm. of the column of liquid was about 1.35 c.c., so that if this heat were not lost from the walls of the tube it would increase the temperature of the solution by about  $0.5^\circ\text{C}$ . in the hour. The previous calculation showed that in order to dissipate this amount of heat a difference of temperature of one-sixth of a degree between the liquid and the air would be necessary.

It may safely be concluded that by taking the temperature of the liquid in the cataphoresis experiments in the way described, an error less than 1 per cent. was introduced into the final calculation, and for the present such accuracy is quite sufficient.

The possibility of convection currents leading to false values for the velocity of the particles has to be considered. Such currents do not affect the result in the way they are liable to do when the motion of a boundary layer is observed—which layer must not be disturbed. During the experiment the concentration of the colloid diminishes at the one electrode and increases at the other. If, by means of convection, any portion of either of these regions of changed concentration should travel up the inverted U-tube so that the concentration  $M$  of the sol changed at the highest point in the tube, then we should naturally deduce a false value for  $v$  (equation 4). Now in the flask in which the concentration increases, the density also increases, and there is no danger of such portion of the liquid passing up the tube. In the other flask the density of the liquid from which the colloid particles have been abstracted by the electric field becomes less. But since this decrease in density originates at the electrode, this portion of the liquid rises immediately, and we should expect it to form a layer of reduced concentration on the top of the liquid in the flask. This was observed very definitely to be the case in every experiment. The upper layer, several millimetres thick, in the flask from which the colloid migrated always became quite colourless, showing that the portion of the liquid from which the colloid was removed rose immediately from the electrode, and showed no tendency to descend to the mouth of the tube.

The actual routine of the transportation experiments with colloidal copper oxide<sup>7</sup> was as follows. As already indicated, the flasks and tube were carefully cleaned. Into each of the flasks was poured 60 to 65 c.c. of the colloidal solution. The inverted U-tube was then inserted in the two flasks placed side by side, and the liquid drawn up to fill the tube. A

<sup>7</sup> The sols used were all prepared by Mr. G. T. R. Evans, to whom I wish to express my thanks.

potential difference (in earlier experiments about 190 volts, later about 240 volts) was applied to the electrodes. The current through the tube was measured by means of a shunted mirror galvanometer, the deflections of which had been calibrated. The current passed for an hour,<sup>8</sup> and then the liquid in the tube was allowed to fall back into the flasks. The two flasks were weighed in order to determine the mass of solution in each case. The solutions were then titrated with standard nitric acid solution in order to determine the amount of colloidal copper present in each.<sup>9</sup> From these measurements can be deduced the amount of colloid per c.c. of the original solution ( $M$ ), and the amount of colloid which has been transported ( $m$ ), both, for simplicity, in terms of the number of c.c. of nitric acid solution required to dissolve the colloid. The value of  $v$  is then calculated for the temperature of the experiment, making use of equation 4. In all cases this value was adjusted to give the velocity of the particles at 20 degrees C., making use of the relation established by Burton that the velocities at different temperatures are inversely proportional to the coefficients of viscosity at these temperatures. The correction necessary amounts approximately to 2·4 per cent. per degree C.

A correction must be applied to the quantity of nitric acid solution required to dissolve the copper in the flasks. In all cases the conductivity of the colloidal solution is due, in the main at any rate, to electrolyte. Since the electrodes are of platinum, one result of the transport is to make the solution in the anode vessel more acid, and that in the cathode vessel more alkaline.\* This obviously affects the titrations, too little nitric acid being required in the anode vessel and too much in the cathode vessel. The amount of acidity and alkalinity produced by the current can easily be calculated, since we can obtain from the galvanometer readings the number of coulombs that have passed. The correction was only 0·01 c.c. of the nitric acid solution for a conductivity of  $2 \times 10^{-6}$ .

In all these experiments with direct current, the observed potential difference—that applied to the electrodes and measured by a voltmeter—was reduced by 1 volt on account of the polarisation *E.M.F.* set up at the electrodes. Another correction to be considered affecting the potential gradient, arises from the fact that there is a gradual current change on account of the electrolyte changes in the two flasks. With solutions of low conductivity, the current always decreased—sometimes by as much as 6 or 7 per cent. in the hour, but usually by about 2 or 3 per cent. Any electrolyte changes in the flasks leading to a fall in the current will involve a reduced potential gradient in the tube, assuming that the liquid in the tube does not change. A corrected potential difference for the experiment can be obtained with sufficient accuracy by multiplying the observed potential difference between the electrodes by the ratio of the

<sup>8</sup> This is about as long as one dare leave it, since some observations (on the movement up the arm of the tube on the cathode side of a slight colour darkening in samples of sol to which rather large quantities of KCl had been added—a darkening due probably to the migration of (OH) ions liberated at the cathode) seemed to suggest that by this time the electrolyte changes at the electrodes were being transported into the neighbourhood of the top of the tube.

<sup>9</sup> Paine, *Koll. Beihefte*, 4, 26 (1912).

\* That is, in so far as the final titrations with nitric acid are concerned. It should be noted that such acidity and alkalinity are almost entirely neutralised at the time they are produced. Free acid dissolves the copper particles, so that the H ions are removed; copper sol is very sensitive to alkali, being quickly coagulated thereby, so that the (OH) ions are strongly absorbed. It is only when the conductivity of the liquid is high that the alkalinity of the liquid in the cathode vessel would become appreciable.

average current to the initial current. This quantity will be proportional to the average potential gradient at the top of the tube.

There was no danger of the constant  $\rho$  (equation 4) being in error on account of a slight displacement of the U-tube up or down relative to the flasks. The position of the tube in the flasks was so chosen that quite a considerable displacement was necessary to produce a measurable effect on the current.

The observations made in these experiments enable us to deduce directly the conductivities of the various sols, making use of equation 3 ( $k = \rho \cdot i/V$ ). All the conductivities detailed in the following tables were obtained in this way.

### Experimental Results.

1. "Pure" Sols.—The following table contains all the results obtained in the experiments with "pure" sols—*i.e.* sols to which no electrolyte had been added. Some of these sols are obviously more contaminated than others, as shown by their conductivities. A comparison of the results from different sols, therefore, will show what is the effect of such contamination.

TABLE I.

Series Number.	Conductivity ( $k$ ) $\times 10^4$	Mobility ( $v$ ) $\times 10^5$	Mass of Copper per Litre (gm.)
C 1	2.03	39.5	0.185
C 2	2.12	39.0	
C 3	2.11	39.0	0.158
D 1	2.19	38.9	
D 2	2.18	39.5	0.250
E 1	0.62	49.7	
E 2	0.48	52.8	0.334
E 3	0.52	51.5	
F 1	0.46	54.1	0.179
F 2	0.46	51.5	
F 3	0.50	50.8	0.204
G 1	1.78	36.8	
G 2	1.88	37.6	0.216
G 3	1.93	41.6	
H 1	0.44	51.2	0.273
H 2	0.52	51.9	
I 1	2.23	41.2	0.273
I 2	2.30	41.4	
J 1	1.48	42.5	0.435
K 1	0.59	50.1	
K 2	0.59	51.6	0.383
M 1	0.72	47.3	
M 2	0.70	48.9	
N 1	1.28	46.6	

Column 1 gives the series number of the experiment. The letter refers to the particular "stock" of copper sol prepared, whilst the number following it refers to the sample drawn from that stock for experiment. Column 2 contains the specific conductivities of the sols (in ohm $^{-1}$  cm $^{-1}$ ), and column 3 the mobilities of the particles (in cms. per sec. per volt per cm.), both calculated for 20°C. In column 4 is recorded the mass of colloid (in grams of copper) per litre of each stock.

In Fig. 2 are plotted the averages of these results. Each point in the diagram represents the average conductivity and mobility of one particular stock of colloidal solution. The values obtained by Burton for copper sols

(brought to 20° C. from the figures given in the paper already referred to) are plotted for comparison. It will be seen that the two sets of data, those obtained by Burton (indicated by crosses) and those deduced from the present experiments (indicated by dots) join on to one another in a satisfactory manner.

Extrapolating to zero conductivity (or to  $0.04 \times 10^{-6}$  the theoretical conductivity of pure water) we should expect a value somewhere between 55 and 60 as the mobility of the particles in pure water. It may be even greater than 60, because the first additions of electrolyte have a more pronounced effect on the velocity of the particles than further additions (see later), and therefore the residual electrolyte impurities in the purest sol examined probably lower the mobility to a considerable extent.

**2. Effect of Electrolytes.**—Measurements were also made of the effect of additions of electrolyte on the velocity of the particles. Experiments of this nature were made originally by Burton. But the most comprehensive series of observations is probably that of Freundlich and Zeh,<sup>3</sup> who measured the velocities of the particles of negative arsenious sulphide sols by Burton's method after various additions of salts had been made. The salts used

were various complex cobalt salts,—chlorides, with positive ions having valencies ranging from 1 to 6. They also experimented with positive ferric oxide sols after additions of potassium salts in which the negative ions ranged from monovalent to tetravalent. The experiments with colloidal copper now to be mentioned gave results which agree with those of Freundlich and Zeh. Curves drawn in the several cases correspond very closely.

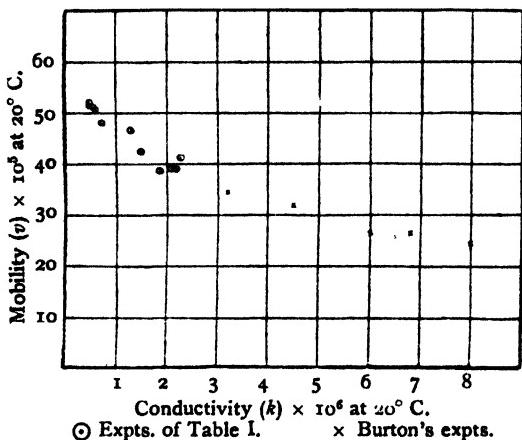


FIG. 2.

In these experiments, the successive additions of electrolyte were made to the stock (litre) flask containing the copper sol, and from this flask the liquid was poured directly into the two experimental flasks. The electrolyte concentrations of the liquid in the stock flask thus gradually increased. The additions were made from a burette, and the electrolyte concentrations were calculated from the burette readings and the successive weights of the stock flask and its contents. For the rest, the method of experiment was the same as for the experiments with "pure" sols. The electrolytes used were KCl, K<sub>2</sub>SO<sub>4</sub>, and K<sub>4</sub>Fe(CN)<sub>6</sub>. Tables II. to IV. contain the results of three sample series. The other series carried out confirmed these very closely.

These results are plotted in Fig. 3. It will be seen that (1) the first additions of salt reduce the velocity of the particles more considerably than later additions do; (2) the greater the valency of the ion carrying a charge opposite in sign to that carried by the particles the greater the effect in reducing the velocity of the particles. Some suggestions as to the significance of these curves will be made in a later section of this paper.

3. *Experimental Notes.*—(a) One rather striking fact was noticed in these experiments. When the sol experimented with had a conductivity less than  $1 \cdot 0 \times 10^{-6}$  or greater than  $3 \cdot 0 \times 10^{-6}$ , no coagulated colloid was deposited on the platinum cathode (the surface of which was vertical), but for conductivities intermediate between these values some coagulated material was always noticed on the cathode at the end of the experiment. This deposit was most "sticky" for conductivities near  $2 \times 10^{-6}$ , requiring rather a lot of shaking of the liquid in the flask for its removal.

(b) With this experimental arrangement, the measurements could be extended into the region in which the colloid is coagulating. For example, in Experiment K<sub>7</sub> (Table III.) the colloid was already coagulating. The stock flask was left to stand for a short while to enable the precipitated material to settle, and the upper portion of the liquid was poured off gently into the transportation flasks; the experiment was then carried out as for other solutions. Suppose now there be any settling taking place during the experiment; the consequence would be that there would be *less* colloid

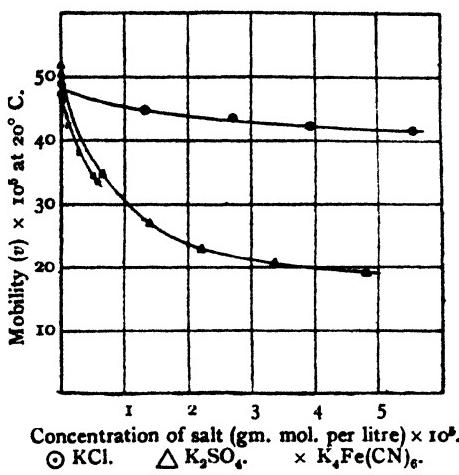


FIG. 3.

TABLE II.

Series M.		Salt — KCl.	Sol. — 0·435 gm. Cu per litre.	
No.	Concentration of Salt gm.-mol. per litre × 10 <sup>5</sup> .		Conductivity (k) × 10 <sup>6</sup> .	Mobility (v) × 10 <sup>5</sup> .
1	—		0·72	47·3
2	—		0·70	48·9
3	1·33		2·65	44·9
4	2·72		4·60	43·5
5	3·91		6·47	42·2
6	5·58		8·85	41·5

TABLE III.

Series K.		Salt — K <sub>2</sub> SO <sub>4</sub> .	Sol. — 0·274 gm. Cu per litre.	
No.	Concentration of Salt gm.-mol. per litre × 10 <sup>5</sup> .		Conductivity (k) × 10 <sup>6</sup> .	Mobility (v) × 10 <sup>5</sup> .
1	—		0·59	50·1
2	—		0·59	51·6
3	0·64		1·77	34·7
4	1·41		3·70	27·0
5	2·22		6·08	23·0
6	3·38		8·83	20·6
7	4·80		12·8	19·2

TABLE IV.

Series N.	Salt — $K_4Fe(CN)_6$ .	Sol. — 0·383 gm. Cu per litre.	
No.	Concentration of Salt gm.-mol. per litre $\times 10^6$ .	Conductivity ( $k$ ) $\times 10^6$ .	Mobility ( $v$ ) $\times 10^4$ .
1	—	1·28	46·6
2	0·122	1·45	42·4
3	0·282	2·00	38·0
4	0·515	2·83	34·4
5	0·582	3·39	33·4

transported, and the calculated result would be too low; in such a case, therefore, the value obtained for  $v$  is a *minimum* value. Similarly, in Experiment N5 (Table IV.), quite a considerable amount of the colloid had been precipitated, and the experiment was carried out with the liquid that had been poured off from the precipitated material.

(c) There appears at first sight to be some discrepancy between these experiments and those of Freundlich and Zeh. The *relative* slopes of the three curves of Fig. 3 are not altogether similar to those obtained in their experiments—the curves for  $K_2SO_4$  and  $K_4Fe(CN)_6$  being too close together. This discrepancy is probably only apparent. The three stocks of colloidal solution, K, M, and N, were prepared on different occasions. They were of different concentrations, and there was no ground for assuming that the sizes of their particles were exactly the same. As we shall see later, the slope of the mobility curve probably depends on the particle size. Hence, stress must not be laid on a quantitative comparison of the copper oxide curves. The curves of Freundlich and Zeh relate to one single stock of colloidal solution and can thus with more reason be compared with one another.

(d) *Accuracy of the Results.*—From an estimate of the accuracy possible in the various measurements it may be concluded that the calculated mobilities are probably correct to within 5 per cent. The three likely sources of error are in the titrations, observations of temperature, and voltage corrections. The titrations could be made to 0·05 c.c. The amounts of colloid transported from the anode region to the cathode region in experiments with pure sols (as detailed in Table I.) varied from 0·75 c.c. for solution D, which was the weakest solution used, to 2·77 c.c. for solution M, which was the strongest. Only in solutions C, D, and G was the total colloid transported equivalent to less than 1·33 c.c. of nitric acid solution. So that except in these three cases, the probable error in the titration results is under 4 per cent. From the discussion on the temperature observations, it may be concluded that an error of half a degree was improbable, this would correspond to an error of a little more than 1 per cent. in the calculated mobility. The voltage correction is certainly of the right order and would not leave an error of more than 1 or 2 per cent. in the final result.

This estimate of the accuracy reached is borne out by the results tabulated in Table I. and plotted in Fig. 2. The agreement between the results for the different solutions is particularly satisfactory for the lowest conductivities. As the conductivity increases we should not expect the different sols to agree too closely, for the effect of an electrolyte on the mobility depends on the nature of that electrolyte, so that as the nature of the contamination might be expected to vary from one sample to another, the plotted results would spread out somewhat as the conductivity increased.

### Ions and Colloid Particles.

There is a growing impression that ions and colloid particles are very much akin, that, for example, there is a fundamental similarity in their electrical structures and in the way in which the application of an electric field causes them to move through a liquid. The fact that the velocities of colloid particles in an electric field are of the same order of magnitude as the velocities of true ions leads one to think of such particles as very large multivalent ions.

The modern theory of ionic mobility throws fresh light on the relation between the colloidal and ionic states, for we now have a more complete picture of the electrical structure of an ion—especially in respect of the effect of an applied electric field in bringing about the motion of the ion. Attention has been called to the fact that the ion is not to be regarded as an isolated charged particle in the liquid. The electrostatic effect of neighbouring ions cannot be neglected, and modern theory has been concerned mainly with deducing the exact nature and extent of this effect.

Debye and Hückel<sup>10</sup> have developed their theory from the idea that the distribution of ions around some one central ion is not an entirely random one, but is determined by the Coulomb law of force as well as by the principles of the general kinetic theory. These neighbouring ions can be regarded as a sort of "ionic atmosphere" around the central ion. At any instant ions of both kinds will form part of the atmosphere of a positive ion, for example, but there will be a preponderance of negative ions. The complete ionic system in each case, therefore, consists of central ion plus ionic atmosphere, and in this system the positive and negative charges exactly balance.

Now, as Debye and Hückel have pointed out, this view of the "structure" of an ion is almost identical with the supposition usually made since Helmholtz with regard to the electrical state of a colloid particle—the supposition of the "double layer." The original idea regarding this double layer was that it formed a parallel plate condenser, the inner surface of which was the surface of the colloid particle, and the outer surface was the surface of the liquid immediately surrounding the particle and separated from it by a distance of the order of  $10^{-8}$  cm. The opposite charges existed on these two opposing surfaces. At the present time, however, while we can picture the inner charge as located on the surface of the particle, we must regard the outer charge as consisting of the *ions* in the liquid, and therefore this outer charge will be diffused through the surrounding liquid. The distribution of the ions around the particle will depend on the electrical attractions and repulsions between the central particle and the ions, and between the ions themselves, and also on the kinetic energy of the ions.

We must conclude, therefore, that the electrical conditions are exactly the same in the two cases—ion and colloid particle—except that in the case of the colloid particle the central charge is very much greater than in the case of the ion, and the ionic atmosphere does not approach as closely to the centre of the system. The structure of the outer portion of the Helmholtz double layer should be identical (except as regards magnitude) with the ionic atmosphere pictured by Debye and Hückel. The mathematical treatment of the two problems must be the same, and we should therefore expect one and the same mobility equation to apply to both ions and colloid particles.

One of the most important conclusions of Debye and Hückel's theory

<sup>10</sup> *Physik. Z.*, 24, 185 and 305 (1923).

relating to ions is that when the concentration of the solution increases, the ionic atmosphere "closes up" as it were on the central ion, and that as a direct consequence of this the mobility of the ion in an electric field diminishes. Thus the molecular conductivity of the solution of an electrolyte decreases as the concentration of the solution increases from zero. The calculation shows that this decrease is directly proportional to the square root of the concentration, in accordance with the empirical rule discovered by Kohlrausch for dilute solutions.

We should expect a similar calculation to be applicable to the mobilities of colloid particles which also are surrounded by ionic atmospheres. In seeking for this application, the following two points should be borne in mind, the one of an experimental, and the other of a theoretical, nature. In the first place, it should be noticed that Debye and Hückel's theory deals primarily with the *mobilities* of the ions. In the case of a true solution these mobilities are often best studied indirectly by means of experiments on the conductivity of the solution. In the case of a colloidal solution, however, the contribution of the colloid particles themselves to the conductivity of the solution is usually quite negligible, and measurements on the conductivity of such a solution will give no information as to the velocity with which the particles are moving. Hence, the mobilities of the particles must be observed directly.

The second point to be noticed is, that, whereas in a true solution the "central ion" is of the same nature (size and charge) as the ions in the atmosphere, in a colloidal solution the "central particle" is quite different (as to size and charge) from the surrounding ions. Consequently, what we describe in the case of a true solution as the study of the variation of the mobility of the ions with the concentration of these ions, becomes in the case of a colloidal solution the study of the variation of the mobility of the particles *with the concentration of the electrolyte in the surrounding liquid*. We shall thus expect to find, for example, that the effect on the velocity of the positive particles of a copper oxide sol produced by the addition of potassium chloride, is of the same nature as the effect on the velocity of the positive (potassium) ions of a potassium chloride solution produced by a similar addition. The concentration of the colloid particles in the liquid—at least in most colloidal solutions of the metal or oxide hydrosol type—does not enter the problem at all; these particles are so far apart from one another that we can neglect any mutual action as far as their migration is concerned.

We now see at once that the state of "infinite dilution" in the case of a true solution becomes, in the case of a colloidal solution, the absence of ions in the liquid surrounding the particles—*i.e.* a solution of zero conductivity. Thinking in terms of the Helmholtz "double layer," we should express this condition by saying that the outer layer is at infinity, since there are no ions in the neighbourhood of the particle. In these circumstances the velocity of the particle in an electric field will be represented by the Stokes equation  $XE = 6\pi\eta bv_0$ , where  $X$  is the electric field applied,  $E$  the charge on the particle, and  $b$  its radius. This equation seems to hold at least approximately for ions; it can therefore safely be applied to colloid particles.

Let us now take Debye and Hückel's general formula for the velocity of an ion (or particle) at any electrolyte concentration.<sup>11</sup>

$$v = \frac{XE}{\rho_b} \left[ 1 - b\kappa - \frac{\rho}{\rho_b} \cdot \frac{E^2\kappa}{6DkT} \right] \quad . \quad . \quad . \quad (5)$$

<sup>11</sup> Debye, *Trans. Faraday Soc.*, **23**, 339 (1927).

where  $\rho_b$  = the "friction constant" of the particle.

$$= 6\pi\eta b. \quad 10 \quad 10$$

$\rho$  = the average "friction constant" of the ions.

$$\kappa = \sqrt{\left(\frac{4\pi}{DkT} \cdot \sum n e^2\right)}.$$

= the reciprocal of the "thickness of the ionic atmosphere," ( $n$  being the number of ions per c.c. in the liquid having charge  $e$ , the summation extending to all the ions).

$D$  = the dielectric constant of the liquid.

$k$  = Boltzman's constant.

$T$  = the absolute temperature.

As already given, we have for zero concentration,

$$v_0 = \frac{XE}{6\pi\eta b} = \frac{XE}{\rho_b}.$$

Hence we have,

$$\frac{v_0 - v}{v_0} = \left[ b + \frac{\rho}{\rho_b} \cdot \frac{E^2}{6DkT} \right] \kappa \quad . \quad . \quad . \quad (6)$$

This corresponds to the expression  $(\Lambda_0 - \Lambda)/\Lambda_0$  for the diminution of the molecular conductivity of a true solution.

In order to make this expression more readily applicable to the experimental study of colloidal solutions, we should notice that  $E$ , the charge on the central particle, is directly proportional to the radius of the particle. (See Stokes' equation above, taken in conjunction with the experimental result that the mobility of the particle is independent of its radius).  $\rho_b$ , the friction coefficient of the particle, is also proportional to the radius of the particle. Hence, equation 6 can be reduced to the form

$$\frac{v_0 - v}{v_0} = ybk \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The quantity  $y$  remains constant as long as we are dealing with one and the same electrolyte. It will also be noticed that the quantity  $b$  depends only on the central particle, and the quantity  $\kappa$  depends only on the surrounding ions.

Debye and Huckel obtained equation 5 on the assumption that the radius  $b$  of the ion was very small. Hückel<sup>12</sup> has extended the theory to the case where the radius  $b$  is not very small, and has thus introduced the factor  $1/(1 + bk)$  into the expression for  $(v_0 - v)/v_0$ . This factor becomes unity, however, when the concentration of the electrolyte is very small, just as when the radius of the particle is very small, and this condition certainly holds for most of the experiments on the migration of colloid particles. Hence, equations 5, 6 and 7 might be expected to hold for these experiments.

The two terms inside the bracket in equation 6 are approximately equal to one another. This will be seen on calculating them when the central particle is a monovalent ion (as in a solution of potassium chloride), in which case  $b$  is approximately equal to  $10^{-8}$  cm.; the two terms remain approximately equal as the radius of the particle increases;  $y$  depends on  $\rho$ , and hence will vary somewhat from one solution to another. Approximately, however, we may write  $y = 2$ .

<sup>11</sup> Physik. Z., 25, 210 (1924); 26, 103 (1925).

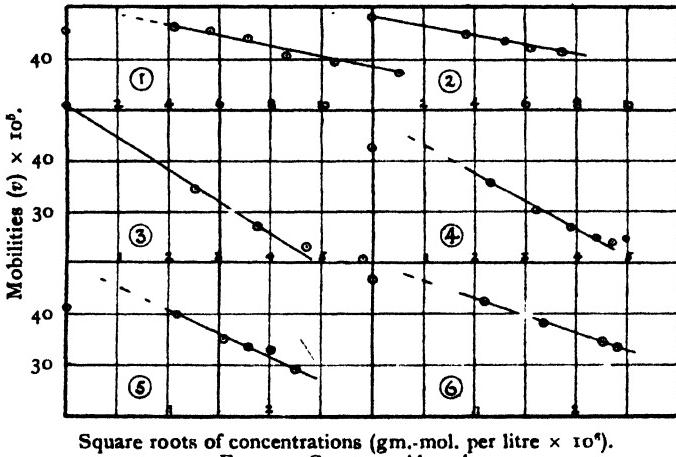
We get a different value for  $y$  if we consider the corrected equation

$$\frac{v_0 - v}{v_0} = \frac{yb\kappa}{1 + b\kappa}$$

At large electrolyte concentrations ( $\kappa$  large), the right-hand side of this equation becomes equal to  $y$ . In these circumstances we might expect  $v$  to vanish, and the left-hand side of the equation to become equal to 1. In any case it will not be greater than 1. On this calculation  $y = 1$ . It may be noticed that, when we are dealing with ions and not colloid particles, the quantity  $b$  in the correcting term  $1/(1 + b\kappa)$ , is really twice the radius of the ion, being the nearest distance of approach of the centre of an outside ion to the centre of the central ion. For colloid particles, however, where the radius is relatively large, we should write this nearest distance of approach as equal to the radius of the particle.

### Experimental Tests.

(1) Equation 7 can now be tested by the experimental data already discussed. In the first place, we should expect  $(v_0 - v)$  to be proportional



Square roots of concentrations (gm.-mol. per litre  $\times 10^6$ ).

FIG. 4.—Copper oxide sol.

to  $\kappa$ , that is, proportional to the square root of the concentration of the electrolyte. Hence, if we plot the mobility of the particles against this square root we should expect a straight line.

This was done for the results obtained with copper oxide sol and for the data given by Freundlich and Zeh in their paper. Figs. 4, 5 and 6 show all these data. The straight lines are drawn so as to pass most closely through the experimental points. The six experiments of Fig. 4 are those tabulated in a previous section of this paper, with "repeat" experiments carried out with the same electrolytes. The electrolytes used in these experiments in order are as follows :

Fig. 4.—Copper oxide sol.

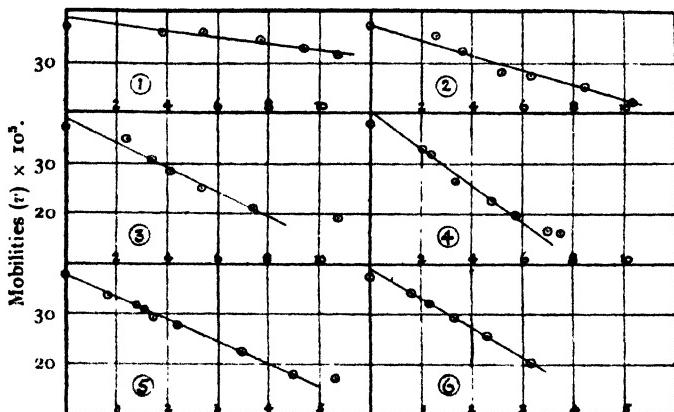
- (1) and (2) KCl, (3) and (4)  $K_2SO_4$ ,
- (5) and (6)  $K_4Fe(CN)_6$ .

Fig. 5.—Ferric oxide sol (Freundlich and Zeh),

- (1)  $KAu(CN)_2$ , (2)  $KAu(CN)_4$ , (3)  $K_2Pt(CN)_4$ ,
- (4)  $K_3Cu(CN)_4$ , (5)  $K_3Fe(CN)_6$ , (6)  $K_4Fe(CN)_6$ .

Fig. 6.—Arsenious sulphide sol (Freundlich and Zeh),  
 (1)  $[\text{Co}]^{\cdot} \text{Cl}$ , (2)  $[\text{Co}]^{\cdot} \text{NO}_3$ , (3)  $[\text{Co}]^{\cdot\cdot} \text{Cl}_2$ ,  
 (4)  $[\text{Co}]^{\cdot\cdot\cdot} \text{Cl}_3$ , (5)  $[\text{Co}]^{\cdot\cdot\cdot\cdot} \text{Cl}_4$ , (6)  $[\text{Co}]^{\cdot\cdot\cdot\cdot\cdot} \text{Cl}_6$ .

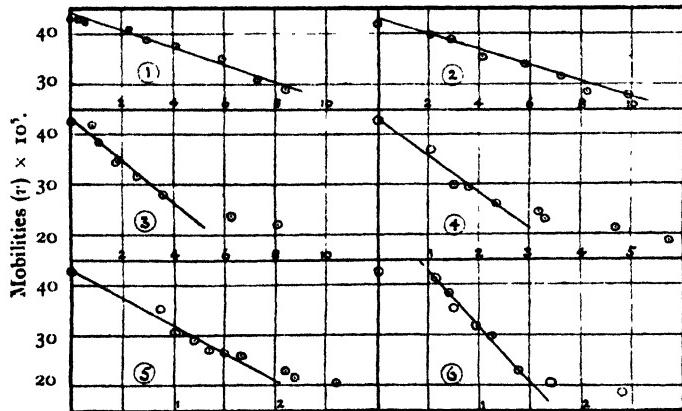
(where  $[\text{Co}]$  stands for a cobalt complex of valency given by the number of "dots" added). It will be seen that the square root law fits very well most of the series of experiments recorded.



Square roots of concentrations (gm.-mol. per litre  $\times 10^6$ ).

FIG. 5.—Ferric oxide sol. (Freundlich and Zeh).

There are two general discrepancies which may be noticed. In the first place, the initial observation often falls below the straight line drawn. This may have something to do with the nature of the residual electrolytes in the original liquid acting in such a manner that the first portion of the added



Square roots of concentrations (gm.-mol. per litre  $\times 10^6$ ).

FIG. 6.—Arsenious sulphide sol. (Freundlich and Zeh).

electrolyte is used up or absorbed, so that the velocity of the particle is not reduced as much as we should expect. It may be the same phenomenon studied by several observers<sup>18</sup> who have noticed an actual increase in the

<sup>18</sup> E.g. Iwanitzkaja and Proskurnin, *Koll. Zeit.*, **39**, 15 (1926); Tendeloo, *Koll. Zeit.*, **41**, 290 (1927).

mobility of the particles on the first additions of an electrolyte. Secondly, there is a tendency for the experimental points to depart from the straight line when the mobility is reduced below a certain value,—the mobility ceasing to diminish as rapidly as the square root law would indicate. But this is exactly what happens for the molecular conductivity curves of the solutions of these same salts.<sup>14</sup> If anything, this "irregularity" emphasises still further the idea that the square root law applies to colloidal solutions *in the same way* that it does to true solutions.

It may be that these curves are not plotted in quite the right way. If some of the electrolyte is "absorbed," the concentrations as given will not be true concentrations in the liquid from which  $\kappa$  is to be calculated. Thus we ought to write  $(v_0 - v)$  as proportional to  $(c - x)$ , where  $c$  is the concentration as calculated from the amount of electrolyte added, and  $x$  is the amount absorbed. This expression becomes  $\propto (1 - x/c)^{\frac{1}{2}}$ . If therefore  $x/c$  is small, (and from absorption experiments we should expect it to become smaller, the greater the concentration), we should still expect a straight line by plotting  $v$  against  $\sqrt{c}$ . But the error would increase as the valency of the absorbed ion increased, since we should then be working with smaller concentrations. No attempt was made to determine  $x$ , and the experimental data are plotted without any correction to  $c$ .

We should conclude from these results that the change in the ionic atmosphere is the probable cause of the change in the mobility of colloid particles on the addition of electrolyte to the sol, just as we now adopt such an explanation for the change in the equivalent conductivity of true solutions. Accordingly, such a change in mobility must not be interpreted as necessarily indicating a change in the electrical charge on the colloid particle. As the concentration of the electrolyte increases, the charge on the particle apparently remains unaltered, and the "ionic atmosphere" contracts.

(2) Equation 7 indicates that  $(v_0 - v)$  should be proportional to  $b$  the radius of one of the particles. Experiments to test this relation have not been carried out. However, we can use the equation for the purpose of calculating the radius of a particle. If we produce the straight line drawn through the experimental points to cut the axis  $\sqrt{c}$ , where  $v = 0$ , we can read off this particular value of  $\sqrt{c}$  and calculate the corresponding value of  $\kappa$ . This is the value of  $\kappa$  which makes  $y\kappa = 1$ . Knowing  $y$  approximately, we can calculate  $b$  the radius of the particle. This has been done in respect of all the curves. The average results for the radii of the particles are as follows :

	$y = 1.$	$y = 2.$
CuO particles	$1.4 \times 10^{-8}$	$0.7 \times 10^{-8}$
Fe <sub>2</sub> O <sub>3</sub> "	$1.2$	$0.6$
As <sub>2</sub> S <sub>3</sub> "	$1.8$	$0.9$

These values are considerably smaller than those usually obtained for colloid particles by methods of counting. Recently, however, Tendeloo<sup>15</sup> has deduced from viscosity measurements, applying a formula of Smoluchowski, the value  $0.6 \times 10^{-8}$  for particles of an arsenious sulphide sol. He attributes such a low result to the presence of very small particles (amicrons) in

<sup>14</sup> E.g., see Fig. 8, later.

the sol which are missed in counting under the ultramicroscope. The two methods of investigation support each other in a remarkable way.

(3) A very striking similarity between the colloidal and ionic states is brought out by comparing Figs. 7 and 8. In Fig. 7 are plotted on the same diagram the straight lines of Fig. 6 (1, 3, and 4) recalculated so that the mobilities at zero concentration should all be 100. All the lines are drawn through this point. In Fig. 8 are given the molecular conductivity curves of the same cobalt salts as were used in obtaining the data of Fig. 7—except that a Cl atom in the divalent cobalt complex is replaced by a (NO<sub>2</sub>) group. These molecular conductivities were measured by Lorenz and Posen,<sup>15</sup> the values at infinite dilution being obtained by extrapolation on a square root concentration diagram. They are calculated to have an initial maximum value of 100. The scales of Figs. 7 and 8 are adjusted to bring out the similarity. The broken line in Fig. 8 is the top line of Fig. 7 drawn to the scale of Fig. 8.

The relative slopes of the three lines are nearly the same in both Figs.

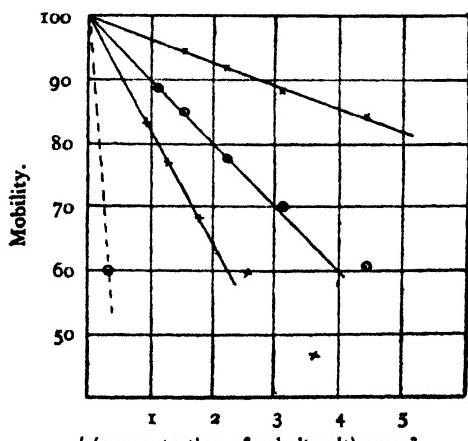


FIG. 8.—Cobalt Solutions.

In Fig. 8, however, the ions whose mobilities we are studying are not the same throughout, the positive ions changing from one line to another, and while the radii of these three positive ions may be the same (as is indicated by the transport ratios obtained for these same salts by Lorenz and Posen),<sup>16</sup> the charges on the ions are certainly different, and, according to

<sup>15</sup> Annual Tables of Constants, vol. iv., p. 948.

<sup>16</sup> *Ibid.*, p. 971.

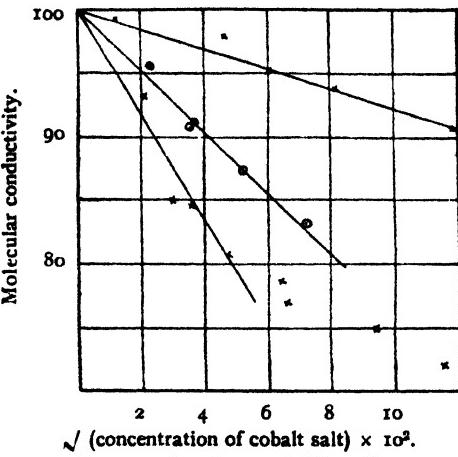


Fig. 7. Arsenious sulphide sols.

The constitutions of the ionic atmospheres are the same for corresponding lines in the two diagrams, but the "central particle" is very much larger in the colloid mobility experiments than in the conductivity experiments—hence, according to Equation 7, the greater steepness of the lines in the former case.

Figs. 7 and 8 are actually more alike than we should expect them to be from the application of Debye and Hückel's equations. In Fig. 7 the central particle whose mobility we are studying is the same for all three electrolytes.

Equation 6, the charge on the central ion has a large effect on the slope of the mobility curve. Put in another way: in passing from one line to another in Fig. 7, we change merely the quantity  $\kappa$  of Equation 6, but in passing from one line to another in Fig. 8, the quantity inside the bracket is affected as well.

(4) There is one great difficulty in applying Debye and Hückel's theory to colloid particles which we have not yet mentioned. According to the theory a salt like  $\text{AlCl}_3$  should have the same effect on the mobility of the particle (positive or negative) as a salt like  $\text{K}_3\text{Fe}(\text{CN})_6$ , for  $\Sigma(ne^2)$  is the same for both; also, the effect of  $\text{K}_2\text{SO}_4$  in reducing the mobility of positive particles should not be of the same magnitude as that of  $\frac{1}{2}\text{Al}_2(\text{SO}_4)_3$ . This is certainly not in accordance with experiment.<sup>17</sup> With colloidal solutions, the effect of a salt in reducing the mobility of the particles, as in coagulating the particles, depends mainly on the nature of the ion of opposite charge to that carried by the particle. As long as  $\kappa$  is to be obtained by taking  $\Sigma(ne^2)$  for all the ions present, it is difficult to see how the Debye and Hückel equation can be used as the sole basis for the explanation of the mobilities of colloid particles.

It is probable that the true ionic concentration in the liquid (outside the spheres of influence of the particles) may be less than that calculated directly from the quantity of electrolyte added to the sol, since some of it is absorbed by the particles. (To what extent the "ionic atmosphere" represents this absorbed quantity is another question arising out of the theory.) But this really makes agreement with experimental observation worse, for the very ions that are known to be most effective in reducing the mobility of the particles are just those which are absorbed most strongly in proportion, leaving relatively less for the surrounding liquid. What we are seeking is an effect by which  $\kappa$ , the reciprocal of the radius of the ionic atmosphere, depends more on the ions of opposite sign to that of the particle than on those of like sign, and absorption seems at first sight to produce the opposite effect. The presence of an excess of the "effective" ion in the ionic atmosphere is already accounted for in the theory as it stands.

One thing seems to be fairly certain, however, that a square root law holds for colloidal solutions as for true solutions in respect of the effect of electrolyte concentration on mobility. This result strengthens the impression that one and the same theory should be applicable to corresponding phenomena in the ionic and colloidal states.

### Summary.

(1) A description is given of a simple form of apparatus for measuring the mobilities of the particles of very pure colloidal solutions of copper oxide by the transportation method, the amount of colloid transported being determined by volumetric analysis.

(2) The highest mobility of copper oxide particles observed was  $52.8 \times 10^{-5}$  cm. per sec. per volt per cm. for a colloidal solution of specific conductivity of  $0.46 \times 10^{-6}$  ohm<sup>-1</sup> cm.<sup>-1</sup>. Extrapolation indicates a mobility of about  $60 \times 10^{-5}$  cm. per sec. for sols of zero conductivity.

(3) A few experiments on the diminution of mobility caused by the addition of electrolyte were carried out. An analysis of these results and of those of Freundlich and Zeh shows that the decrease in mobility from the

<sup>17</sup> See for example Burton, loc. cit., ref. 2, p. 590.

value at zero electrolyte concentration is directly proportional to the square root of the concentration of the electrolyte.

(4) The application of Debye and Hückel's theory to colloidal solutions is discussed, and some indications are given of the effect of the size of the central particle on the diminution of mobility produced by electrolytes. Some suggestions are made as to the bearing of this, as well as of the above square root rule, on the relation between the colloidal and ionic states.

*Note added June 22nd.*—Since correcting the proof-sheets of the above, I have seen a paper by Hans Müller (*Koll. Beihete*, **26**, 257, April, 1928) on the Theory of the Electric Charge on a colloidal particle and its evaluation from the electrokinetic potential as determined by experiments on cataphoresis. Starting from the assumption of the "diffuse double layer" (the "ionic atmosphere" in Debye and Hückel's theory), he develops a graphical method for deducing the charge on the particle and the radius of the particle. He also has examined the results of Freundlich and Zeh's experiments on arsenious sulphide sol, and concludes that in this particular sol the "charge" on the particle remained constant on the addition of electrolyte. He deduces the value  $1.58 \times 10^{-6}$  cm. as the average radius of the particles of this sol.

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## SOLUTIONS. PART I.—THE FREEZING-POINT DIAGRAMS AND LATENT HEATS OF EVAPORATION OF BINARY MIXTURES OF VOLATILE LIQUIDS.

BY WILFRED FISHER WYATT.

(Received 1st June, 1928.)

Binary liquid mixtures may be classified as (1) normal systems, the properties of which follow very closely the additive laws, and, (2) abnormal systems, the properties of which deviate from the additive laws. The causes of the deviations have been considered by Dolezalek,<sup>1</sup> Hildebrand,<sup>2</sup> and Weissenberger,<sup>3</sup> who have discussed the possible nature of the forces operating between the different species of molecules in the mixtures. The thermal properties of binary liquid mixtures have been examined from time to time with the object of elucidating the nature of these forces, but owing to the methods used for the calculation and expression of the results obtained in certain cases, characteristic irregularities in the curves have not been manifested. The thermal property which should throw most light on these forces, but yet has hitherto not been examined to any extent, is that of the latent heat of evaporation. It was pointed out by Tyrer<sup>4</sup> that if association, or solvation, or compound formation occurs between the molecules of a binary liquid mixture, some energy change is to be expected dur-

<sup>1</sup> Dolezalek, *Z. physik. Chem.*, **64** (1908), 727.

<sup>2</sup> Hildebrand, "Solubility," *Amer. Chem. Soc.*, monograph, p. 72.

<sup>3</sup> Weissenberger, *J. prakt. Chem.*, **115** (1927), 78.

<sup>4</sup> Tyrer, *J. Chem. Soc.*, **99** (1912), 1633; **101** (1912), 81, 1104.

ing this process, and this energy change should affect the value of the latent heat of the mixture. Tyrer accordingly carried out accurate measurements of the latent heats of evaporation, the boiling-points, and the composition of the saturated vapour phase in equilibrium with the liquid phase at varying concentrations, for the following systems : acetone-chloroform, carbon tetrachloride-ethyl alcohol, benzene-ethyl alcohol, chloroform-methyl alcohol, carbon tetrachloride-ethyl acetate, carbon tetrachloride-ether, ethyl bromide-benzene, and benzene-chloroform.

In calculating his results, Tyrer obtained the latent heat per gram of the mixture, and related this quantity graphically to the weight per cent. of one of the components. The latent heats per gram of the mixtures, however, are not comparable quantities, since the number of molecules present varies with the molecular weights of the components and the concentration of the mixture. The quantities required for the purpose of comparison are the molal latent heats, and when this method of expressing the results is employed, characteristic irregularities become apparent in the curves showing molal latent heat plotted against the molecular percentage of one of the components. The method used for the recalculation of Tyrer's results was as follows :—

Suppose we have a solution of two volatile components *A* and *B*, the concentration of *A* being *x* weight per cent., and suppose that from this solution one gram of vapour be evaporated, the heat supplied being *H* calories, the *L<sub>p</sub>* quantity of Tyrer. The composition of the vapour is not necessarily the same as that of the solution from which it came. Let the composition of this vapour be *y* per cent. by weight of *A*. The number of gram molecules of *A* in one gram of the vapour is given by the expression  $y/100M_A = a$ , where *M<sub>A</sub>* is the molecular weight of the component *A*. The corresponding number of gram molecules of *B* is given by  $(100 - y)/100M_B = b$ , where *M<sub>B</sub>* is the molecular weight of the component *B*. Then the total number of gram molecule in one gram of the mixed vapour is  $(a + b)$ , and since *H* is the total latent heat per gram, the *total molal latent heat* of the mixture of the above composition is  $H/(a + b)$  calories. The *internal molal latent heat* of the mixture, which is a measure of the work done in enabling one gram molecule of the vapour to escape from the liquid phase, can now be obtained from the total molal latent heat, assuming that the gas laws hold for the mixture, by subtracting the quantity *RT* calories, where *R* is the gas constant and *T* the boiling-point in degrees absolute. Since the maximum variation in boiling-points for the systems considered in the present communication is approximately 14°, the error introduced by assuming the validity of the gas laws for these mixtures is not of sufficient magnitude to affect the general form of the molal latent heat curves. Figs. 2 to 5 show the internal molal latent heats for the systems acetone-chloroform, carbon tetrachloride-ethyl alcohol, benzene-ethyl alcohol, and benzene-chloroform respectively, plotted against the molecular percentage of one of the components. The full lines show this relationship with reference to the liquid phase, and the broken lines with reference to the vapour phase.

The results obtained by Williams and Daniels<sup>5</sup> for the specific heats of mixtures of acetone and chloroform have been recalculated in the same manner, and the curves showing molal heat capacity plotted against the molecular percentage of chloroform in the mixtures are shown in Fig. 6.

In order to elucidate the possible causes of the irregularities in the

<sup>5</sup> Williams and Daniels, *J. Amer. Chem. Soc.*, 47 (1925), 1490.

above curves, the freezing-point diagrams for the four systems have been investigated, and these are shown together with the above curves in Figs. 2 to 5.

### Experimental.

The liquids used were purified by standard methods and fractionally distilled immediately before use. The ethyl alcohol was dried, first by refluxing over freshly burnt quick lime, and afterwards by treatment with aluminium amalgam. All precautions were taken to ensure that the liquids were not contaminated with moisture.

Since the liquids under investigation freeze at very low temperatures, a special modification of the ordinary freezing-point apparatus was adopted, as illustrated in Fig. 1. The mixture was placed in a jacketted test tube immersed in a cooling bath, the whole being supported at the bottom of a large unsilvered Dewar tube, and any desired quantity of liquid air could be introduced into the bottom of the Dewar tube from a liquid air flask. The liquid air flask was provided with ordinary wash bottle fittings and pressure was developed in it by means of a sprayer bulb. Stirrers were provided for both the mixture under observation and the liquid in the cooling bath. Absolute alcohol served as the bath liquid for temperatures down to  $-110^{\circ}$ , and below this temperature the system of air jackets alone was used, the rate of cooling in this case being controlled by suspending the system at a suitable height in the Dewar tube. A pentane thermometer, graduated in degrees from  $0^{\circ}$  to  $-200^{\circ}$  was used for all temperatures below  $-80^{\circ}$ , but for temperatures above  $-80^{\circ}$  a standard alcohol thermometer was used. Since the liquids were clear, the appearance of solid in the mixtures was easily detected and thus acted as a check on the values of the freezing-points obtained from the cooling curves. Owing to the possibility of contamination by moisture a fresh mixture was made up for each freezing-point determination.

Undercooling at the freezing-point was minimised by introducing into the mixtures crystals of the solid obtained by freezing a small quantity of the liquid in a capillary tube placed in the liquid air.

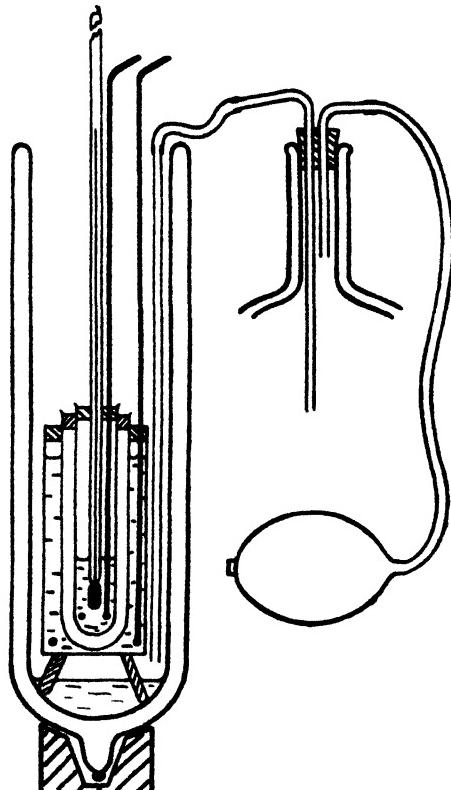


FIG. 1

### Results.

(1) *Acetone-Chloroform Mixtures.*—For low concentrations of chloroform in the liquid phase,\* the internal molal latent heat shows small but increasing positive deviations from the straight line joining the values of the latent heats of the pure components, as the concentration of chloroform is increased. At 50 per cent. the curve shows a change of slope, and for concentrations greater than this the molal latent heat increases rapidly to a maximum value at 82 per cent., from which it falls to the value for pure chloroform.

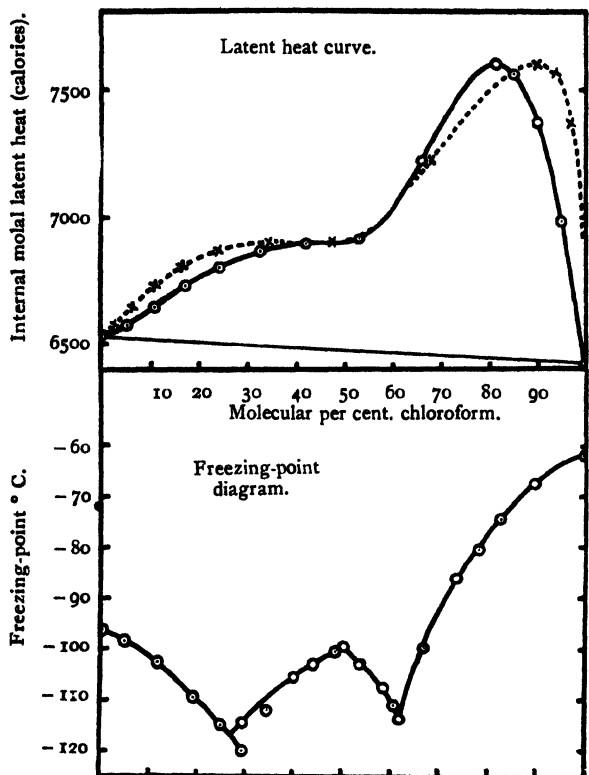


FIG. 2.—Acetone-chloroform.

The freezing-point diagram for this system shows that a stable compound is formed between one molecule of acetone and one molecule of chloroform, as is indicated by the sharp maximum at 50 per cent. The melting-point of the compound is  $-99.5^{\circ}$ , and the two eutectics occur at 27 per cent. of chloroform, temperature  $-117^{\circ}$ , and 62 per cent. of chloroform, temperature  $-114^{\circ}$  respectively.

(2) *Ethyl alcohol-Carbon tetrachloride Mixtures.*—For concentrations up to 33 per cent. of carbon tetrachloride, the latent heat curve follows very closely the straight line joining the values of the latent heats of the pure components, and for concentrations

greater than 33 per cent. the latent heat rises very slightly to a maximum value at about 45 per cent. and then decreases. Between 15 and 69 per cent. of carbon tetrachloride the curve shows positive deviations, and between 69 and 100 per cent. negative deviations with a minimum value at 95 per cent.

The freezing-point diagram shows a transition point at 44.6 per cent. of carbon tetrachloride, temperature  $-47.6^{\circ}$ , the eutectic temperature being  $-118^{\circ}$  at 11 per cent. of carbon tetrachloride.

(3) *Ethyl alcohol-Benzene Mixtures.*—For low concentrations of benzene the value of the internal molal latent heat increases slightly to a maximum value at 2.5 per cent. For concentrations greater than 2.5 per cent. of

\* All concentrations given refer to molecular percentage in the liquid phase, except where otherwise stated.

benzene the value of the latent heat decreases, and at 20 per cent. the curve exhibits a sudden change of slope. The curve shows positive deviations from the straight line joining the values of the latent heats of the pure components between 0 and 9.7 per cent., and between 60 and 100 per cent., and negative deviations between 9.7 and 60 per cent. of benzene.

The freezing-point diagram for this system was investigated by Pickering<sup>6</sup> over the temperature range above  $-80^{\circ}$ , but in view of the possible occurrence of a transition point, as in the case of ethyl alcohol-carbon tetrachloride mixtures, which exhibit a similar molal latent heat curve, the freezing-point diagram was again investigated. No transition point was, however, observed. The eutectic point occurs at 2.5 per cent. of benzene, temperature  $-118^{\circ}$ .

(4) *Benzene-Chloroform Mixtures.*— From 0 to 50 per cent. of chloroform the value of the internal molal latent heat shows a gradual increase, and from 50 to 100 per cent. the value falls to that for pure chloroform, the whole of the curve showing positive deviations from the straight line joining the values of the internal molal latent heats of the pure components.

The freezing-point diagram shows that the system gives a normal curve exhibiting an eutectic point at 73 per cent. of chloroform, temperature  $-79^{\circ}$ .

### Discussion.

Reference to the diagrams shows that in the systems examined, those giving a molal latent heat curve deviating irregularly from the straight line joining the values of the latent heats of the pure components give freezing-point diagrams which have other features than a simple eutectic point. The system which gives a simple eutectic freezing-point diagram gives also a regular molal latent heat curve.

<sup>6</sup> Pickering, *J. Chem. Soc.*, **63** (1893), 998.

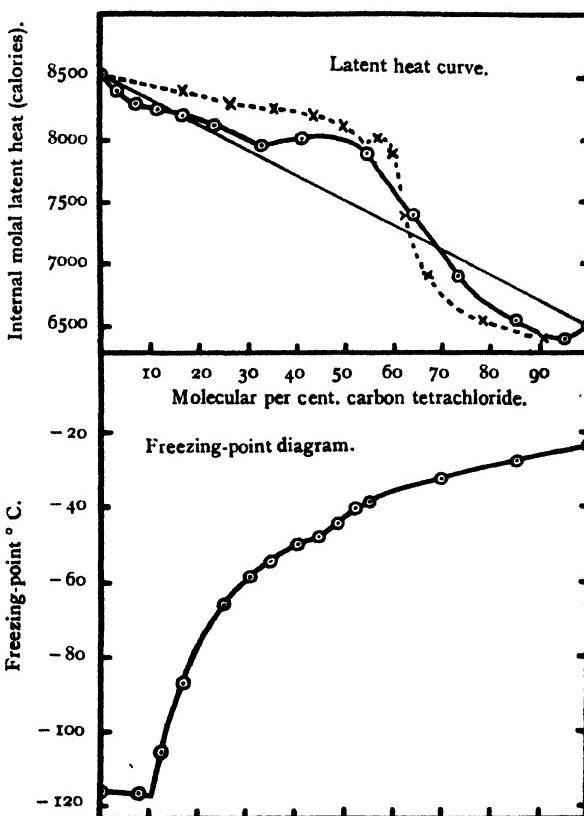


FIG. 3.—Ethyl alcohol-carbon tetrachloride.

The explanation advanced by Dolezalek, that the minimum in the vapour pressure curve for the system acetone-chloroform is due to the formation of a chemical compound between one molecule of acetone and one molecule of chloroform is shown by the freezing-point diagram to be correct. The heats of mixing for this system have been shown by Carroll and Mathews<sup>7</sup> to be positive at the boiling-points of the mixtures, indicating that relatively strong forces of attraction exist between the two species of molecules, even at elevated temperatures. This is confirmed by the fact

that the internal molal latent heat curve shows positive deviations throughout the entire range of concentrations. The marked rise in the value of the internal molal latent heat for concentrations greater than 50 per cent. of chloroform indicates that the compound is much more stable in excess of chloroform than in excess of acetone. As shown in Fig. 6 the relative increase in the value of the molal heat capacity over the range of concentrations between 50 and 100 per cent. of chloroform may be attributed to the same cause, since such increased stability would result in an increased absorption of heat due to the breaking down of the compound as the temperature was raised.

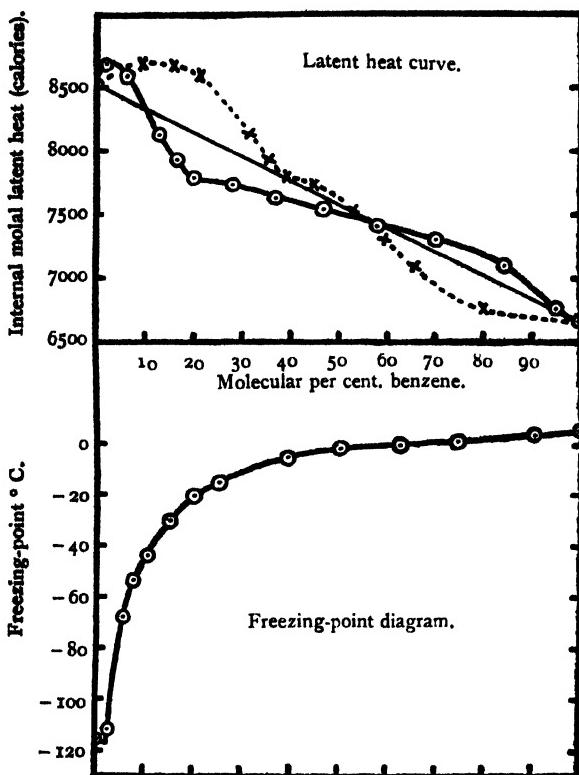


FIG. 4.—Ethyl alcohol-benzene.

The systems ethyl alcohol-carbon tetrachloride and ethyl alcohol-benzene may be considered together since they exhibit marked similarities. Reference to the values of the internal molal latent heats of the pure components shows that in both cases large differences occur, these differences being 2012 calories in the case of ethyl alcohol-carbon tetrachloride, and 1852 calories in the case of ethyl alcohol-benzene. The high value for ethyl alcohol has long been attributed to the association of the molecules present in the pure liquid. The internal molal latent heat curve for each system shows a sudden change of slope. The essential difference between the curves is that the deviations from the straight line joining the values of the latent heats of the pure components in the two cases are reversed, in that where one shows positive deviations the other shows negative deviations and *vice versa*.

<sup>7</sup> Carroll and Mathews, *J. Amer. Chem. Soc.*, 46 (1924), 30.

The freezing-point diagrams also show similarities, for when they are plotted together on the same scale it is seen that the lowering of the freezing-point of either benzene or carbon tetrachloride by the addition of ethyl alcohol is very small, both curves running parallel for concentrations between 0 and 45 per cent. of ethyl alcohol. Similarly the lowering of the freezing-point of ethyl alcohol by the addition of either carbon tetrachloride or benzene is small, and in both cases the eutectic point lies well over to the pure alcohol side. The only difference between the general forms of the curves is that a transition point occurs in the case of ethyl alcohol-carbon tetrachloride but not in the case of ethyl alcohol-benzene. It would therefore appear that the forces operating between the molecules in both systems are essentially similar, the difference being one of degree only.

The form of the internal molal latent heat curves is not explained by the views of Dolezalek. If positive deviations of the vapour pressure curve are due to dissociation of the complex alcohol molecules on the addition of the second component, then the latent heat curve should show negative deviations from the additive law, since on evaporation, a smaller quantity of heat would be required to liberate the alcohol molecules from the liquid phase. A slight decrease in the case of ethyl alcohol-carbon tetrachloride is observed for low carbon tetrachloride concentrations, but in the case of ethyl alcohol-benzene an increase occurs for low benzene concentrations. Further, if the explanation advanced by Dolezalek applied, then a regular change in the value of the internal molal latent heat with concentration would result, but this change is found to be irregular.

The view of Weissenberger, that positive deviations of the vapour pressure curve may be due to forces of repulsion operating between the molecules is open to criticism if applied to systems such as those under consideration. For since forces of attraction exist between molecules of the same species, it is probable that any forces of repulsion between molecules of the different species would cause a separation into two layers.

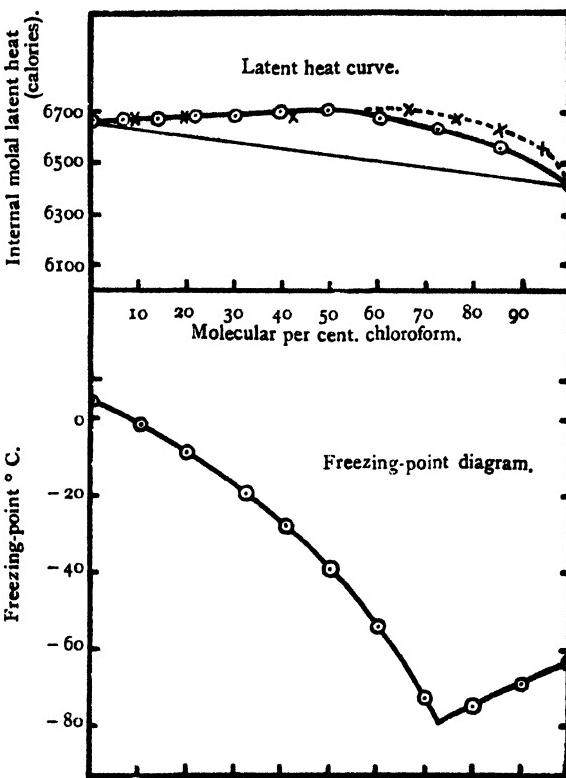


FIG. 5.—Benzene-chloroform.

It may be that the explanation of the above systems is to be found in terms of the Internal Pressure theory, and further experiments, designed to test its applicability to the elucidation of the results, are in progress.

A sudden change of slope in the internal molar latent heat curve occurs for the system ethyl alcohol-benzene at the molecular ratio 1 benzene to 4 ethyl alcohol in the liquid phase, and for the system ethyl alcohol-carbon tetrachloride at the molecular ratio 1 carbon tetrachloride to 2 ethyl alcohol in the liquid phase. The cause of these changes of slope is at present not clear, but it may be that the forces which are operating between the two species of molecules at the boiling-point can be measured in some kind of units of molecular force.

In order to investigate whether or not the abnormally low depressions of the freezing-points in the above cases are due to the formation of solid solutions, the solid phases separating out from the mixtures on freezing were isolated and analysed. The liquid was removed from the freezing mixtures by a capillary pipette, and the solid was then freed from adherent

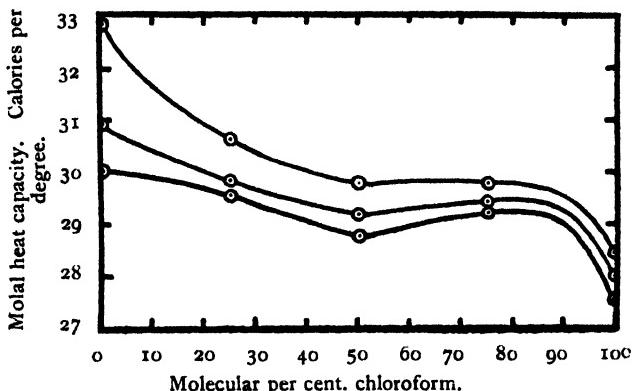


FIG. 6.—Acetone-chloroform.

liquid by stirring and pressing it with a drying tube, made by placing absorbent wool for a distance of 5 inches along a glass tube and plugging the end with glass wool, this being protected by a piece of silk. Gentle suction was applied by means of a water pump during this process. The solid was then withdrawn, allowed to melt, brought to 20° C. in a thermostat, and analysed in a refractometer. Since the removal of the final traces of mother liquor is a matter of considerable difficulty, a high degree of accuracy was not expected for the values of the composition of the solids thus obtained. They were however consistent, and on plotting gave smooth curves. In the case of ethyl alcohol-benzene the results indicated that alcohol separates out along with the benzene, the solidus curve being almost a straight line between 0 per cent. of alcohol at the freezing-point of benzene and 30 per cent. of alcohol at -27°. From this point the curve falls rapidly to 47 per cent. of alcohol at the eutectic temperature, the form of the curve being convex to the temperature axis.

In the case of ethyl alcohol-carbon tetrachloride the solidus curve obtained was almost a straight line between 0 per cent. of ethyl alcohol at the freezing-point of carbon tetrachloride, and 20 per cent. of alcohol at the transition temperature, and almost a straight line between 25 per cent. of

alcohol at the transition temperature and 54 per cent. of alcohol at the eutectic temperature. In this system the difference in the concentrations of the conjugate solid solutions at the transition temperature is therefore of the order of 5 per cent. Confirmation of this comparatively small difference was afforded by the length of time during which the temperature remained constant at the transition point during the cooling of the mixtures. These times were 4·5 minutes for the 48·1 initial per cent. of carbon tetrachloride mixture, and 6 minutes for the 51·8 initial per cent. of carbon tetrachloride mixture, the temperature of the bath being 4° lower than that of the mixtures.

In the system benzene-chloroform, the internal molal latent heat curve is distinct in type from those of the systems previously considered in that it exhibits no irregularity. It shows positive deviations throughout the entire range of concentrations, which may be interpreted as indicating that relatively strong forces of attraction exist between the two species of molecules. The freezing-point curve is seen to be of the simple eutectic type, and the analysis of the solids separating out from the freezing mixtures indicates that two series of solid solutions exist, one on either side of the eutectic point. The solidus curve on the benzene side is slightly convex to the temperature axis and runs from 0 per cent. of chloroform at the freezing-point of benzene to 30 per cent. of chloroform at the eutectic temperature. At high chloroform concentrations the solidus curve runs from 0 per cent. of benzene at the freezing-point of chloroform to 10 per cent. of benzene at the eutectic temperature. It is also of interest to note that the vapour pressure curve for this system shows negative deviations from Raoult's law but does not exhibit a minimum value.

### Summary.

(1) In order to investigate the forces operating between the molecules of the components of binary liquid mixtures preliminary considerations of the latent heats have been made. The results of Tyrer have been recalculated to show the changes of internal molal latent heat with concentration for the systems acetone-chloroform, ethyl alcohol-carbon tetrachloride, ethyl alcohol-benzene and benzene-chloroform, and marked changes of slope in the curves have been observed in the first three systems.

(2) A similar change of slope has been observed for the system acetone-chloroform when the molal heat capacity is plotted against the molecular percentage of chloroform in the mixtures.

(3) The freezing-point diagrams for the above four systems have been investigated, and in the case of acetone-chloroform a compound is formed between one molecule of acetone and one molecule of chloroform, melting-point - 99·5°. For the system ethyl alcohol-carbon tetrachloride a transition point occurs on the liquidus curve at 44·6 per cent. of carbon tetrachloride, temperature - 47·6°. The system ethyl alcohol-benzene shows no transition point, but the curve is displaced considerably to the ethyl alcohol side. A normal eutectic curve was found for the system benzene-chloroform.

(4) The solids separating out from the freezing mixtures have been isolated and analysed, and extended series of solid solutions are indicated for the systems thus examined. The transition point in the case of ethyl alcohol-carbon tetrachloride is due to conjugate solid solutions, the difference

in molecular concentrations of these at the transition temperature being of the order of 5 per cent.

(5) The views of Dolezalek, Weissenberger, and Hildebrand are briefly considered in relation to the above results.

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## THE ABSORPTION SPECTRUM OF IODINE IN ETHYL ALCOHOL.

BY ALAN BATLEY.

(Received, 4th June, 1928.)

The results of investigations by previous workers, on the absorption spectrum, in the visible and ultra-violet regions, of iodine dissolved in ethyl alcohol show a marked lack of agreement.

Thus Waentig<sup>1</sup> states that iodine dissolved in ethyl alcohol does not show the usual band in the blue or green region of the spectrum which is characteristic of iodine in most other solvents (chloroform, carbon disulphide, benzene, etc.) and in the vapour state, but instead, exhibits a heavy absorption throughout the ultra-violet with maxima at  $360\mu\mu$  and  $290\mu\mu$  approx. (values deduced from Waentig's graphs), of a type not shown by solutions in chloroform, etc.

Crymble, Stewart, and Wright,<sup>2</sup> however, recorded an absorption maximum in the visible region at  $480\mu\mu$ , of the type usually characteristic of iodine, with only slight absorption in the near ultra-violet, but increasing in the further ultra-violet to a second maximum at  $303\mu\mu$ . This latter band apparently corresponds to Waentig's band at  $290\mu\mu$ .

According to Massol and Faucon,<sup>3</sup> an iodine solution in ethyl alcohol shows three maxima—a band in the visible at  $470\mu\mu$  (compare Crymble, Stewart, and Wright— $480\mu\mu$ ) and absorption throughout the ultra-violet with maxima at  $350\mu\mu$  and  $288\mu\mu$ . All three maxima were also observed and measured by Stobbe and Schmidt.<sup>4</sup>

Later, Lowry and Sass<sup>5</sup> have published results contradicting those of Massol and Faucon but similar to those of Crymble, Stewart, and Wright, in that they record a visible band at  $477\mu\mu$ , no band-head in the neighbourhood of  $350\mu\mu$ , but a second maximum at  $290\mu\mu$  of about four times the intensity of the visible band.

The results of Brode<sup>6</sup> support the statement by Waentig, but differ completely from those of all other workers. He found no absorption maximum in the visible, but heavy absorption throughout the ultra-violet with maxima at  $361\mu\mu$  and  $292\mu\mu$ . Furthermore, his observations as to the intensity of the far ultra-violet band give a value more than three times that of Lowry and Sass.

Work in disagreement with the observations of Waentig and of Brode, but in agreement with all the others, has been published by Ornstein and Bürger,<sup>7</sup> and by Gróh,<sup>8</sup> their investigations being confined to the visible

<sup>1</sup> *Z. physik. Chem.*, **68**, 513 (1910).

<sup>2</sup> *Ber.*, **43**, 1183 (1910).

<sup>3</sup> *Compt. rend.*, **164**, 813 (1917).

<sup>4</sup> *Z. wiss. Photogr.*, **20**, 57 (1920).

<sup>5</sup> *J. Chem. Soc.*, **622** (1926).

<sup>6</sup> *J. Amer. Chem. Soc.*, **48**, 1877 (1926).

<sup>7</sup> *Proc. Amsterdam Acad.*, **29**, 573 (1921).

<sup>8</sup> *Z. anorg. Chem.*, **162**, 287 (1927).

region of the spectrum. They quote results indicating that iodine in ethyl alcohol shows an absorption maximum in this region of the type usually characteristic of the iodine molecule, the values for  $\lambda_{\max}$ . as measured by them being respectively  $445\mu\mu$  and  $447\mu\mu$ .

Apart from the discrepancies described above, between the various published results, there is further discordance in the explanations put forward by those observers who did record high extinctions throughout the ultra-violet, as to the origin of this absorption. Thus, Waentig attributes it to the presence of solvated iodine, that is, addition products of iodine and ethyl alcohol; Massol and Faucon look upon it as characteristic of the normal iodine molecule, while Stobbe and Schmidt suggest that formation of hydriodic acid in the solution produces hydrogen polyiodides exhibiting ultra-violet absorption. In no case is experimental evidence supplied as direct proof of the particular conception.

It seems certain, from other observations by Waentig and by Hildebrand and Glascock<sup>9</sup> that iodine does form an addition compound, or solvate, with ethyl alcohol, but there is no proof that this solvate formation is directly responsible for the ultra-violet absorption, although this is assumed, by these authors, to be the case. Similarly, although the presence of hydriodic acid (and, therefore, presumably of polyiodides) in an old solution of iodine in alcohol has been observed by Schwarzi,<sup>10</sup> it has not yet been shown that such compounds are in fact responsible for the spectroscopic anomalies.

Since consideration of the suggested explanations has been neglected by the later workers, it was considered of importance to ascertain the actual cause of the discrepancies above referred to, and to determine the true absorption curve of iodine dissolved in ethyl alcohol.

### Experimental Procedure.

*Apparatus.*—Most of the observations described in this paper were made with the aid of a Hilger ultra-violet quartz spectrograph used in conjunction with a Hilger sector-photometer. The dispersion given corresponds to a distance of about 20 cms. on the photographic plate between wavelengths  $210\mu\mu$  and  $700\mu\mu$ , the distance between  $210\mu\mu$  and  $400\mu\mu$  being about 16 cms.

The light source used with this spectrograph was a quartz mercury vapour lamp enclosed by a mask having a circular hole coinciding with the end of the lamp. This light source, although it has the disadvantage of showing a few intense emission lines, which, unless care is taken to give suitable length exposures, tend to "fog" the plate, has the following advantages. The photograph of its spectrum shows a continuous "background" of almost uniform intensity from the visible throughout the ultra-violet as far as the plates record. Unlike the ordinary arc or spark in air, it does not require constant readjustment during the experiment, and furthermore, emits light at a constant intensity. This last quality, as will be seen later, was a necessary one for the investigations described here.

The more detailed examination of the visible part of the absorption spectrum was carried out with another spectrograph calibrated to cover the spectrum from  $400\mu\mu$  to  $1500\mu\mu$ , corresponding to a distance of 18 cms. on the photographic plate, the distance between  $400\mu\mu$  and  $600\mu\mu$  being about 11 cms. A sector-photometer is used, as with the ultra-violet apparatus and the light-source is the positive crater of a carbon arc, whose

<sup>9</sup> *J. Amer. Chem. Soc.*, 31, 27 (1909).

<sup>10</sup> *Pharm. Presse*, 30, 60 (1925).

spectrum, as registered on an Ilford panchromatic plate (which with normal exposures is sensitive up to about  $720\mu\mu$ ) is ideal for spectrophotometry in this region.

By means of the sector-photometer, two comparison beams of light from the same light-source, each passing through an absorption cell and a rotating sector, are focussed on the slit of the spectrograph to be finally registered on the photographic plate as two spectra in close juxtaposition. One of the absorption cells contains the experimental solution and the other the pure solvent, so that any difference between the two spectra as finally registered, must be due to absorption by the solute. The ratio of the sector-openings, and, therefore, of the amounts of light-energy passing through the sectors, is adjustable to known values. If for a certain value of this ratio, the wave-lengths are determined at which the intensities of the two photographed spectra are equal, then, for these wave-lengths, the value of  $\log (I_0/I)$  is given directly by the sector-reading, where

$$\log (I_0/I) = e.c.d.,$$

where "e" = extinction coefficient, "c" = concentration of solute in moles per c.cm., and "d" = cell-thickness in cms.

By taking a series of photographs, with varying sector-readings, the whole absorption curve may be determined.

With regard to the absorption cells used, the usual types, in which the end-plates are either cemented on, or pressed on by screw-caps and washers, were found to be unsuitable. The cells actually used throughout this work are of 2·15 cms. internal thickness and are made wholly of quartz, with fused-on end-plates, and fitted with a side-tube.

Since it has been suggested, by earlier workers, that we are dealing with chemical equilibria of some kind, it follows that, to obtain precise measurements, temperature-control of the cells is desirable. The chief difficulty when a sector-photometer is used is that, owing to the construction of the photometer, the tubes are set at an angle and are also too close together to allow of them being fitted with separate jackets. Furthermore,

it is necessary, with such short cells that the temperature, not only of the side-walls, but also of the end of the tubes, should be efficiently controlled.

In the arrangement used by the present writer both cells  $C_1$  and  $C_2$  (Fig. 1) are enclosed completely in a single water-jacket, J, kept at  $25^\circ$  C. by circulation from a large constant-temperature reservoir. The jacket consists essentially of a brass box, having suitably arranged and parallel quartz windows, W, to permit the passage of the two beams of light. The cells are held by means of rings, R, and elastic bands in sockets in a brass holder, D, which may be removed from the jacket when adjusting the cells. The sockets in the holder are cut in such a way as to allow the respective rays to pass axially through the cells. The side-tubes of the cells reach well above the level of the water and are closed by rubber tubing and clips. X and Y in the figure are respectively the inlet and outlet of the water-jacket.

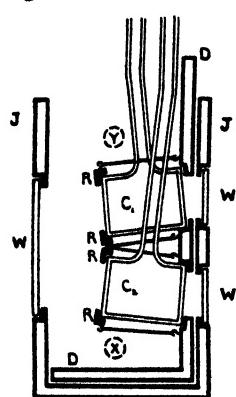


FIG. 1.—The absorption cells and heating jacket.

and clips. X and Y in the figure are respectively the inlet and outlet of the water-jacket.

It should be mentioned that a very slight inaccuracy in making the cell

holder, or in adjusting the plane of the quartz windows can lead to an appreciable error in the photometer readings. Probably for this reason, it was found necessary, with the ultra-violet apparatus, to apply a correction of  $0.03$ , constant for all wave-lengths, to the sector-readings. Thus, for example, a sector-reading of  $1.5$  will correspond to  $\log (I_0/I) = 1.47$ .

With the visible spectrographic apparatus, no correction was required.

*Purification of the Ethyl Alcohol.*—Absolute alcohol was digested in a mechanical shaker for fifteen hours with freshly calcined lime. It was then decanted off and fractionally distilled. The whole operation was repeated twice.

### The Absorption Spectra.

In using the sector-photometer, the procedure normally followed by the present writer was to take photographs at all sector-readings,  $0.0$ ,  $0.1$ , . . .  $1.4$ ,  $1.5$ , in turn, and then immediately afterwards to duplicate the photographs in the reversed order. The wave-lengths of the points of

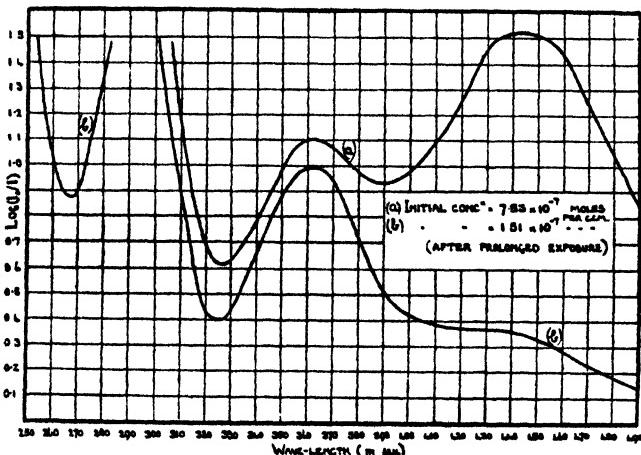


FIG. 2.—Effect of light on the absorption by solutions of iodine in ethyl alcohol.

equal intensity of the two comparison spectra were then found for each photograph, the mean of results from duplicate photographs for each sector reading being used in the graph, in which wave-length ( $\lambda$ ) is plotted against  $\log (I_0/I)$ .

Using this method to examine a solution of iodine in ethyl alcohol of concentration  $7.53 \times 10^{-7}$  moles per c.c., it became obvious, from comparison of the two photographs taken at different times with any one sector-reading, that the absorption curve undergoes a change with time, there being a gradual increase in the absorption in the ultra-violet beyond about  $440\mu\mu$ . Thus the points on the  $\log (I_0/I) - \lambda$  graph deduced from the various photographs do not correspond to the same state of the changing absorption curve. For each sector-reading, however, the mean of the results from the two duplicate photographs will correspond to the same state of the absorption curve as that at which the photograph with sector set at  $1.5$  was taken, since the time of taking this latter photograph was approximately midway between those of taking the former two. The curve obtained from such mean values is shown in Fig. 2, curve (a), and represents

the absorption at the instant of taking the photograph with sector set at 1·5. The curve shows maxima at  $444\mu\mu$  ( $\log (I_0/I) = 1\cdot52$  approx.) and  $363\mu\mu$  ( $\log (I_0/I) = 1\cdot10$  approx.), and heavy absorption, above the range of the sector-readings, in the further ultra-violet. The first of these maxima, which lies just within the visible range of the spectrum, is of the same type, and of similar magnitude, with that normally shown by iodine in other solvents (Ornstein and Bürger).<sup>7</sup>

Measurements with a solution of one-fifth of the concentration of the above, showed that with prolonged exposure to the mercury lamp, the absorption curve became more nearly constant and gave readings shown in Fig. 2, curve (b), the original maximum at  $444\mu\mu$  being overshadowed by absorption with maxima at  $362\mu\mu$  and  $291\mu\mu$ .

It was noted that the ultra-violet absorption of another sample of this dilute solution, which had been kept in darkness, had not changed to so great an extent as that which had been exposed to the mercury lamp, but that it at once began to increase on exposure.

It may be concluded then, from the above preliminary experiments, that in solutions of iodine in alcohol, changes take place giving rise to increased absorption in the ultra-violet showing maxima at  $362\mu\mu$  and  $291\mu\mu$ , which eventually overshadow the maximum shown initially at  $444\mu\mu$ , these changes being largely, if not wholly, of photochemical origin.

*The Possible Causes of the Changes in Absorption Spectrum.*—Let us consider the possible chemical causes of these changes in absorption spectrum.

(1) The suggestion that the behaviour is to be attributed to slow solvation of the iodine after dissolution seems extremely unlikely, as the process of solvation is usually taken to be practically instantaneous, and furthermore, thermal, rather than photochemical.

(2) There is the possibility that a more definite series of chemical reactions is proceeding, the results of which may be classified in two groups, (a) oxidation products, and (b) substitution products.

(a) Direct substitution in the alcohol by iodine is unlikely, but slow oxidation may be taking place with formation of acetaldehyde or even acetic acid, and hydriodic acid. The hydriodic acid formed, could of course combine with iodine to give polyiodides. The formation of oxidation products such as acetaldehyde, acetic acid and ethyl acetate has actually been detected by Schwarzi.<sup>10</sup>

(b) Iodine substitution products may be formed by action of iodine on the above oxidation products (this process also being probably accompanied by formation of hydriodic acid.) In this connection, it may be mentioned that, according to Shafer,<sup>11</sup> the action of bromine on alcohol may give rise to formation of bromal, ethyl bromide, or bromoform, so that the possibility of formation of any of the corresponding iodo-substitution products must be considered.

We have now to attempt to correlate the absorption changes with certain of the above compounds. By reference to measurements of the absorption by organic halogenated molecules (Lowry and Sass,<sup>5</sup> Crymble, Stewart and Wright,<sup>2</sup> Scheibe,<sup>12</sup> Landolt-Bornstein Tabellen), our attention is drawn to iodoform, since this is the only molecule which shows two band-heads of the type required, the values of  $\lambda_{\text{max.}}$  being stated by Lowry and Sass to be  $345\mu\mu$  and  $294\mu\mu$  and by Crymble, Stewart, and Wright, to be  $357\mu\mu$  and  $303\mu\mu$  respectively.

With regard to the possible formation of hydrogen polyiodides, the

<sup>11</sup> Ber., 4, 366 (1871).

<sup>12</sup> Ber., 58, 586 (1925).

absorption spectrum of hydrogen tri-iodide in water has been measured by Winther<sup>13</sup> who found it to exhibit two maxima, at  $353\mu\mu$  and  $290\mu\mu$ , that is, of a similar nature to those of iodoform.

*Isolation of the Absorbing Reaction-product.*—To obtain more direct evidence in the present case, the following experiment was carried out.

It was found that the absorbing reaction-product which we seek to identify could be isolated in the solid form by allowing a film of a solution of iodine in alcohol to evaporate on a layer of gelatin on a glass plate (an unexposed photographic plate, thoroughly fixed, washed and dried, being used). The crystalline deposit of iodine can easily be brushed off, but there remains a brown deposit which apparently is impregnated in the gelatin. That this deposit is actually the reaction product which was present in the original iodine solution is indicated by the following facts:—

(1) No such brown deposit is formed in the gelatin if a solution in chloroform, carbon bisulphide or any solvent in which iodine shows a normal spectrum, be used.

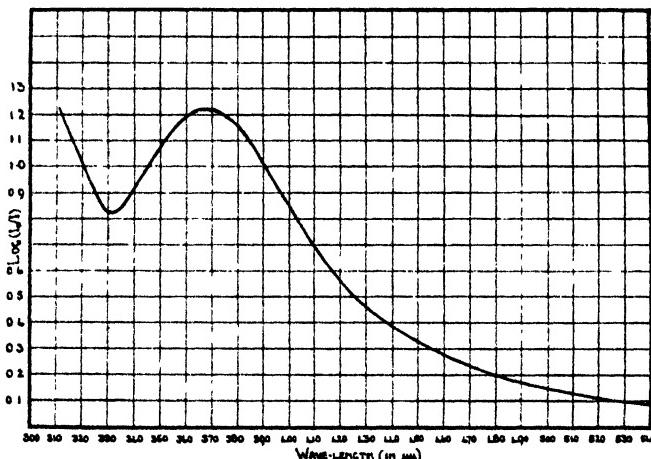


FIG. 3.—Absorption by the deposit on gelatin from a solution of iodine in ethyl alcohol.

(2) The extent of formation of the brown deposit from an alcoholic solution is less from a freshly made solution than from an old one.

(3) Its absorption spectrum is of the nature expected.

The absorption of the stained plate was measured, with the usual absorption cells and heating jacket removed, but with another unstained part of the same plate in the comparison beam, observations being necessarily restricted to the near ultra-violet due to the heavy absorption by glass and gelatin. The results are shown in Fig. 3, and, although only one maximum, at  $368\mu\mu$  can be measured, it is obviously of the nature which would be expected, from the preliminary experiments, for the reaction product. There is a slight displacement to greater wave-lengths; such a shift is to be expected when a substance passes from solute to solid form.<sup>14</sup> There is no trace in the curve of the characteristic iodine maximum in the neighbourhood of  $444\mu\mu$ .

It may be emphasised once more that the gelatin has been used merely as a physical method of separating the compound from the alcohol solution,

<sup>13</sup> Z. physik. Chem., 108, 236 (1924).

<sup>14</sup> Ribaud, Ann. de Phys., 12, (9), 107 (1919).

and not as a chemical reactant. It was found that although the deposit was only removed relatively slowly by washing with water, yet with a solution of sodium thiosulphate, the gelatin was immediately decolorised, thereby indicating that the complex pre-formed in the alcoholic solution is rather an unstable addition compound than an iodo-substituted organic molecule. It has already been indicated that of these addition compounds, hydrogen triiodide, as suggested by Stobbe and Schmidt, is the most probable.

*Experiments in the Presence of Ozone.*—Let us now consider the effect of adding an oxidising agent to the iodine solution.

If the reaction giving rise to the absorption changes is merely formation of a solvate as suggested by Waentig then the rate of such changes would not be affected by the presence of the oxidising agent. If the formation of organic oxidation products from the alcohol (2(a) above) or the formation of substitution products from these organic oxidation products, is the origin of the absorption changes, then the rate of the changes would be accelerated, since the oxidising agent would give increased formation of acetalde-

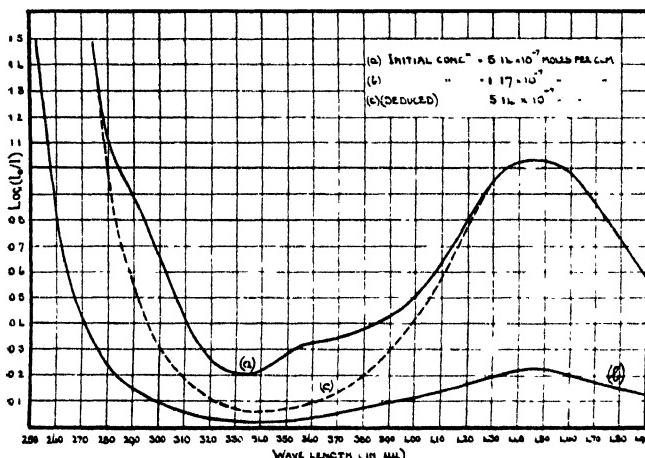


FIG. 4.—Absorption by iodine solutions in ethyl alcohol in the presence of ozone.

hyde, etc. Lastly, if the absorption is due to polyiodides formed by combination of the iodine with hydriodic acid as the latter is produced, then the rate of development of the ultra-violet bands would be diminished since the oxidising agent would tend to decompose the hydriodic acid.

Experiments have been carried out using ozone as the oxidising agent, the alcohol being saturated with the gas immediately before making up the iodine solution. A preliminary experiment showed that the ozone itself absorbs too far in the ultra-violet to have any effect on the measurements made. Solutions of two concentrations were examined ( $5.14 \times 10^{-7}$  moles per c.c. and  $1.17 \times 10^{-7}$  moles per c.c. respectively), and the results are shown in Fig. 4, curves (a) and (b).

It will be seen that in the dilute solution, formation of the two maxima at  $291\mu\mu$  and  $362\mu\mu$  is entirely suppressed, while with the concentrated solution, there is, at these wave-lengths, merely a slight inflection of the curve, whose only maximum is at  $446\mu\mu$ . One would naturally expect the ozone to be more efficient in its action in the more dilute iodine solutions since here it is in a relatively greater excess. It may therefore be

taken as proved, that the change with time, in the ultra-violet absorption of iodine solutions is due to the absorption by hydrogen polyiodides gradually formed.

It would seem to be a safe deduction to say that the true curve for the more concentrated iodine solution should be more of the nature of curve (c) (dotted curve, Fig. 4). Such a curve indicates the absorption spectrum by free iodine in ethyl alcohol solution to be exactly analogous, both in shape and in order of magnitude of the band, to its absorption in normal solvents such as chloroform, carbon tetrachloride, etc.

A more detailed examination of the absorption in the visible region in the presence of ozone was carried out by use of the visible spectrographic apparatus, the maximum being found to be at  $447\mu\mu$ . In connection with this small but definite discrepancy in the value of  $\lambda_{\text{max.}}$  as found by the two spectrographs, it should be realised, that since the formation of polyiodides is photochemical, its rate will be influenced by the distribution of the radiation in the spectrum of the light source used. Now, whereas the radiation density for the carbon arc is fairly uniform throughout its spectrum, it has been shown by Cunliffe, Franklin, Maddison and Reeve<sup>15</sup> that about 15 per cent. of the total radiation energy of the mercury lamp is emitted at the line of wave-length  $435\mu\mu$ , which wave-length is very near the absorption maximum of molecular iodine. It is therefore to be expected that hydrogen iodide will be formed more readily under the influence of the mercury lamp than of the carbon arc. Furthermore, it is obvious that increase in the ultra-violet absorption by polyiodides will, due to the overlapping of the bands, cause an apparent shift to smaller wave-lengths, of the iodine band, so that the discrepancy between the results from the ultra-violet and visible apparatus is quite well explained, the more correct value for  $\lambda_{\text{max.}}$  for iodine being therefore  $447\mu\mu$  with a value for  $\epsilon_{\text{max.}}$  of  $9.54 \times 10^6$ .

*More Detailed Study of Absorption-time Relations.*—Since it has been shown that the formation of hydrogen triiodide is taking place, we must have the reaction



followed by



the former being slow and photochemical, and the latter probably a practically instantaneously reached thermal equilibrium. The amount of hydrogen triiodide present at any instant will be measured by  $K[\text{I}_2] \cdot [\text{HI}]$ , where  $K$  is the equilibrium constant of reaction (2).

If these reactions proceed without any complications, the concentration of the triiodide  $[\text{HI}_3]$  (and the consequent absorption in the ultra-violet) will pass through a maximum, being zero when  $[\text{HI}]$  is initially zero, and approaching zero again when  $[\text{I}_2]$  finally approaches zero. On the basis of mass action considerations, it can be shown that the maximum concentration will occur at some time between the iodine being one-third decomposed and being one-half decomposed, according to whether the value of  $K$  approaches infinity or zero.

To determine whether a maximum in the concentration of triiodide occurs or not, it was necessary to make a more detailed study of the manner in which the absorption curve of iodine in pure alcohol changes with time. It was therefore necessary to devise a method whereby the true absorption curve at any particular time may be determined for a

<sup>15</sup> *J. Physical Chem.*, 30, 1427 (1926).

rapidly changing solution (since it is impossible experimentally to make measurements at all sector-readings simultaneously) and also the rate of change in the extinction at any wave-length.

If we consider the manner in which a gradual change in an absorption curve will be registered on a series of photographs taken over a series of time-intervals with the same sector-reading, it becomes obvious that the points of equal intensity will vary in position (that is, in wave-lengths). Two points on either side of an absorption maximum would gradually move further and further apart on the wave-length scale if the absorption were increasing or would draw closer together if the absorption were de-

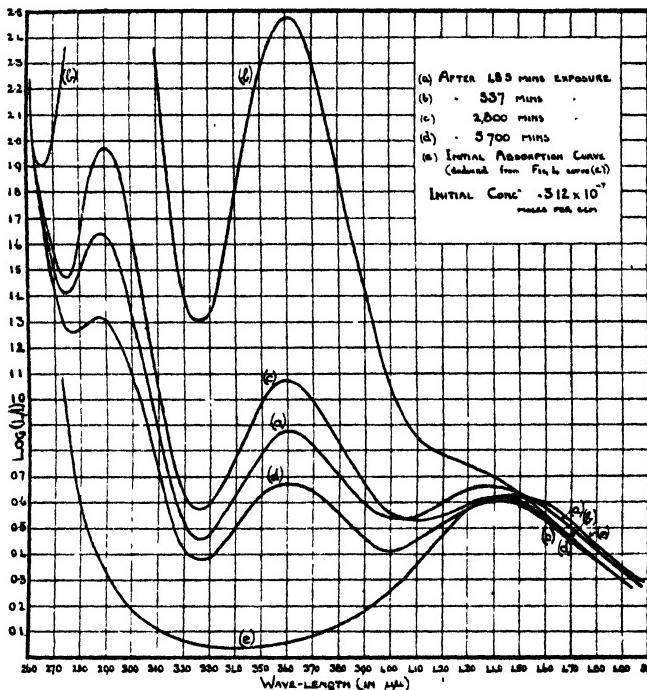


FIG. 5.—Change, with time, in the absorption by a solution of iodine in ethyl alcohol.

creasing. The converse would take place if the two points considered were on either side of an absorption minimum.

The method used was to take photographs, noting the time at half exposure;\* and working through the range of sector-readings, and then repeating the measurements at suitable time-intervals according to the rate at which the curve is changing. Thus there results, for each sector-reading used, a series of wave-length values, for various known times, of the points of equal intensity. These wave-length values are plotted against the time to form a curve from which the wave-lengths of points of equal intensity at any intermediate time may be deduced. If these curves for all the sector-readings be plotted on the same graph, then in this graph we have the three quantities  $\lambda$ ,  $\log (I_0/I)$ , and  $t$ , so that from it we may deduce (a) the true absorption curve at any instant (that is, the  $\log (I_0/I) - \lambda$

\* That is, a photograph with an exposure occupying the time interval from  $t$  to  $t + \Delta t$  is assumed to be equivalent to a reading taken instantaneously at the time  $t + \Delta t/2$ .

curve) and (b) a curve, for any wave-length, showing the change in intensity of absorption with time (that is, the  $\log(I_0/I) - t$  curve). (Actually, if  $t$  = minutes from time of half-exposure of the first photograph taken, the quantity  $\log(t+1)$  was used in the graphs for these experiments since it gives more proportionate curves.)

The experiments were carried out in a room darkened, except for the spectrographic light-source, as far as possible, the solutions being made up rapidly in flasks blackened on the outside and used immediately after making. The solutions were shielded from the direct rays of the mercury lamp whilst being transferred to the cell, and were not exposed until the time of taking the first photograph. These precautions were taken in order that the starting-point should be as close as possible to the initial state of wholly undecomposed iodine. A current of 2 amperes, adjusted by means of an external variable resistance, was used in the lamp, the fluctuations in amperage being quite negligible.

For an iodine solution initially of concentration  $3.12 \times 10^{-7}$  moles per c.c., the actual absorption curves (that is,  $\log(I_0/I) - \lambda$  curves)

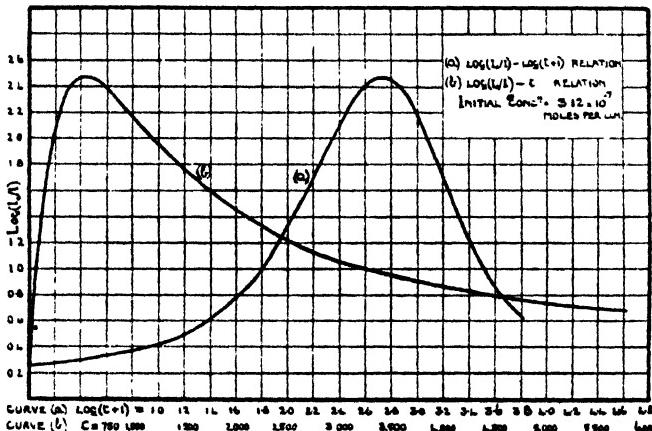


FIG. 6.—Change, with time, in the intensity of the absorption at wave-length  $360\mu\mu$ .

exhibited at various instants, as deduced by the method described above, are shown in Fig. 5, curve (a), (b), (c), and (d). Also included in Fig. 5, is a curve (curve (e)) deduced from Fig. 4, curve (c), as being the true absorption curve for free iodine of concentration,  $3.12 \times 10^{-7}$  moles per c.c.

Curve (a), Fig. 6, is the deduced  $\log(I_0/I) - \log(t+1)$  curve for wave-length  $360\mu\mu$ ; that is, it shows the manner in which the intensity of the tri-iodide band at  $360\mu\mu$  changes with time (or, more strictly, with  $\log(t+1)$ ). That part of the curve lying above a value of 1.97 for  $\log(I_0/I)$ —that is, above the range of the sector-readings, has been deduced by comparison with similar  $\log(I_0/I) - \log(t+1)$ , curves for neighbouring wave-lengths for which the extinction, not having passed above the range of the sector-readings, was accurately known, and also by reference to the results of other measurements, not quoted in this paper, of the hydrogen tri-iodide absorption curve. Curve (b), Fig. 6, is the  $\log(I_0/I) - t$  curve for the same wave-length ( $360\mu\mu$ ) plotted in terms of  $t$  (rather than  $\log(t+1)$ ), the nature of the changes being more easily appreciated when shown in this way.

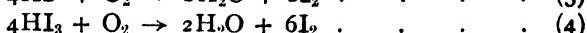
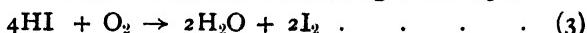
Now, by comparison of curves (*b*) and (*e*), Fig. 5, it is obvious that the molecular extinction of iodine at  $360\mu\mu$  is negligible compared with that of hydrogen tri-iodide, so that curves (*a*) and (*b*), Fig. 6, may be taken as representing the manner in which the amount of tri-iodide present changes with time.

Examination of the figures shows that, as expected, the amount of tri-iodide present passes through a maximum, the time taken to reach this maximum ( $t_{\max.}$ ) being 537 minutes, or practically 9 hours. At this point of the reaction the absorption by the tri-iodide, with band-heads measured as being at wave-lengths  $290\cdot5\mu\mu$  and  $360\cdot5\mu\mu$  respectively, quite masks that of the free iodine present (Fig. 5, curve (*b*)). Contrary to expectation, however, it is seen that as the tri-iodide absorption passes its maximum, and in time gradually approaches zero, the original iodine band, namely, at  $447\mu\mu$ , instead of approaching zero also, reappears with almost the original intensity (actually, after 95 hours continuous exposure, about nine-tenths of the latter—compare Fig. 5, curve (*d*)). It necessarily follows that not only is the amount of hydrogen tri-iodide present at any instant before  $t_{\max.}$  (Fig. 6) limited by the concentration of hydriodic acid, but it is also limited at times later than  $t_{\max.}$  by the same factor, and not by the concentration of iodine. That is, the amount of hydrogen tri-iodide present never reaches the maximum predicted earlier on the assumption that reactions (1) and (2) are proceeding free from other complicating factors, but passes through an earlier maximum, due to the effect of some other influence not yet considered.

Incidentally, it may be seen from Figs. 5 and 6, that at times later than  $t_{\max.}$  the rate of change in the amount of hydrogen tri-iodide present is so slow that it is sufficiently accurate to plot experimentally found absorption curves direct, without applying the above described method of correction, and solutions, having reached this almost steady state, or false equilibrium, might easily give the impression of having a quite stable and constant absorption curve (as must have been the case with some of the observers mentioned earlier).

To explain the re-formation of the iodine, we must consider what other reactions may take place subsequent to or simultaneous with reactions (1) and (2).

Winther<sup>13</sup> has shown, for aqueous solutions, that both hydriodic acid and hydrogen tri-iodide are oxidised by dissolved oxygen, the oxidation being partly thermal and partly photochemical. Now, the solubility of oxygen in water at *N.T.P.* is of the order of  $15\cdot2 \times 10^{-7}$  moles per c.c. Since the solubility in ethyl alcohol is about five times as great (Seidell, "Solubilities"), then, in the solution used in the experiment described, the molar concentration of oxygen present would be of the order of twenty-five times that of the total iodine, so that oxidation according to the equations



may be expected to be considerable, especially under the influence of radiation so strong in the ultra-violet as that from a mercury lamp.

Furthermore, in the presence of any water initially present (only a minute concentration may be necessary), or formed during reactions (3) and (4) we may also have



Lastly, there is the possibility of iodine reacting with acetaldehyde, or, more probably, acetic acid, to give organic substitution products, thus

causing a gradual diminution of the total iodine present either in the free state or as hydrogen iodides. Such reactions, probably complex, may be classified together as reactions (6).

With regard to reactions (1) and (5), since hydriodic acid is itself a strong reducing agent, we may assume that there will also be, to some extent, back reaction in these cases, although, on the other hand, there is unlikely to be any appreciable opposing effect in reactions (3) and (4).

Initially, then, formation of hydriodic acid will commence at a certain rate by reaction (1) and possibly reaction (5), which would tend to attain a definite equilibrium state, or photostationary state, corresponding to some definite ratio between the concentrations of iodine and hydriodic acid. The rate of formation of tri-iodide, by rapid reaction (2) will be governed, in these first stages, by the rate of formation of hydriodic acid. The presence of this reaction (2), removing equimolar quantities of iodine and hydriodic acid, will itself produce a retarding effect on the rate of reaction (1) (from left to right).

If reactions (1) and (2) alone were proceeding undisturbed, and if the extent of the formation of hydriodic acid corresponding to the photo-stationary state, were sufficiently advanced, then, in the manner described earlier, the amount of hydrogen tri-iodide present (and the consequent absorption in the ultra-violet) would pass through a maximum, being limited initially (when  $[HI]$  is small), by the amount of hydriodic acid present, and finally (when there is excess hydriodic acid) by the amount of iodine present. Let a maximum formed in this (hypothetical) manner in the  $\log (I_0/I)$ -time curve for the  $360\mu\mu$  band-head be referred to as of type A.

Actually, however, there are factors which will tend to disturb this course. As the concentration of hydriodic acid and hydrogen tri-iodide increase, reactions (3) and (4) will take place in increasing extent, to give back the original iodine, until eventually the opposing effects on the value of the ratio of iodine to hydriodic acid will balance, the ratio being temporarily constant. This state, however, will be only transient for the following reason. Although the concentration of hydriodic acid is temporarily constant, the concentration of the organic oxidation products continues to increase, so that the back reaction to the oxidation of the alcohol (equations (1) and (5)) will continue to increase, equilibrium thus corresponding to a smaller and smaller concentration of hydriodic acid. The ratio of iodine to hydriodic acid, instead of approaching zero, will therefore pass through a minimum and commence to increase again.

If this state occurs before that which would give rise to the maximum of type A, above, that is, if this minimum value of the ratio  $[I_2]/[HI]$  is greater than that value which, if we had simply reactions (1) and (2) proceeding undisturbed, would give maximum formation of tri-iodide, then formation of this minimum for the term  $[I_2]/[HI]$  would itself produce a maximum in the term  $[HI_3]$  (and therefore in the  $\log (I_0/I)$ -time curve for wave-length  $360\mu\mu$ ). The maximum thus formed in the  $\log (I_0/I)$ -time curve for  $360\mu\mu$  will then be of a different type (type B) from that already considered (type A) in that the concentration of tri-iodide, as measured by the absorption at  $360\mu\mu$ , on both sides of the maximum is limited by the concentration of the hydriodic acid. The state towards which the solution finally tends will thus be one in which the concentration of iodine approaches its original value and those of hydriodic acid and hydrogen tri-iodide approach zero.

Briefly, the whole mechanism may be described as follows:—

In a solution of iodine in pure alcohol, quite free from dissolved oxygen, the iodine would eventually be completely converted into hydriodic acid,

the concentration of tri-iodide passing through a maximum for some value of the term  $[I_3]/[HI]$  depending on the value of the equilibrium constant. It will be shown later that, even in the presence of dissolved oxygen (which actually would be extremely difficult to avoid) the changes in the solution will follow a similar course so long as ultra-violet radiation is excluded.

On the other hand, if exposed to ultra-violet radiation (as from the mercury lamp), then in the presence of dissolved oxygen, oxidation of the hydrogen iodides will tend to check and eventually, to reverse the process of formation of hydriodic acid and hydrogen tri-iodide, whose concentrations thus both pass through a maximum, the state finally approached being that of complete re-formation of the original iodine, which thus passes through a cycle of reactions the net result of which is the oxidation of the alcohol by the dissolved oxygen.

Thus a satisfactory explanation of the results given in Figs. 5 and 6, may be supplied on the basis of this mechanism, the fact that the absorption by the iodine restored at the end of the 95 hours exposure is only about nine-tenths of the initial value indicating that, to a slight extent, reactions (6) are also entering. Incidentally, it is quite possible that organic oxidation or substitution products may eventually be formed in sufficient amount to affect the far ultra-violet absorption in some way.

In the experiment, described earlier, in which ozone was present in the solution, reactions (3) and (4) would be considerably accelerated so that a maximum of type B would be set up much earlier in the decomposition of the iodine, only a small amount of tri-iodide having been formed. This, of course, is exactly as was obtained.

*Effect of Dilution.*—It has been shown that there are, in the iodine solutions under the influence of the mercury lamp, photochemical reactions opposing one another. Furthermore, we may expect that, unless the reactions are of the same order, their relative velocities will vary with the dilution of the solution. That is, the relative magnitude of the opposing effects on the value of the ratio  $[I_3]/[HI]$  will vary in some way, depending on the actual orders of the opposing reactions (which orders, since the reactions are photochemical, need not be the same as would be expected from the stoichiometric equations) with the dilution of the solution.

The results of the actual investigations carried out in this section indicate that the reactions producing hydriodic acid give, under the influence of the mercury lamp, a higher order of reaction than those producing iodine, so that the velocity of the latter relative to the former increases with increasing dilution. That is, the oxidation reactions in the dilute solutions overpower the reactions involving decomposition of the iodine more rapidly and at an earlier stage in the formation of hydriodic acid (and hydrogen tri-iodide) than in the more concentrated solutions. Thus, with increasing dilution, there is a decrease in the value of  $t_{\max}$ . and the intensity of the tri-iodide absorption (relative to the initial concentration of iodine) at time  $t_{\max}$  also decreases. For example, the absorption spectrum of a solution of concentration  $0.74 \times 10^{-7}$  moles per c.c. had attained a steady state that is,  $t_{\max}$ . had been reached, in less than an hour, the intensities of the  $360\mu\mu$  and  $447\mu\mu$  maxima being represented by  $\log (I_0/I) = 0.32$  and  $0.14$  respectively. Thus, the absorption at  $360\mu\mu$  is only about twice that at  $447\mu\mu$  as compared with four times in Fig. 5, curve (b).

*Effect of Pre-exposure to Daylight.*—A further experiment, of interest in connection with the dependence discussed earlier of the velocity of a photochemical reaction on the light-source used, was carried out.

The solar radiation is well known to be weak in the far ultra-violet, where hydriodic acid absorbs, and it is therefore to be expected, that if an iodine solution were exposed to sunlight in a glass vessel (which would still further cut out ultra-violet light) then the velocities of reactions (3) and (4) may possibly become quite small compared with those of reactions (1) and (5). The solution may thus possibly show the behaviour, discussed in the first considerations, as being the simplest possible, in that the formation of hydriodic acid may proceed to such an extent that the  $\log (I_0/I)$  - time curve for the tri-iodide band-head ( $360\mu\mu$ ) may actually show a maximum of type A. That is, the iodine in the solution may eventually approach complete conversion into hydriodic acid, and this the actual experiment proved to be the case.

Another portion of the same solution as was used in the last experiment (concentration  $0.74 \times 10^{-7}$  moles per c.c.) was exposed to bright daylight in a glass flask for several hours. The absorption curve was then measured and the value of  $\log (I_0/I)$  found to be 0.56 at  $360\mu\mu$ . A current of pure, dry oxygen was then passed through the same solution for about 30 minutes, thus accelerating the decomposition of hydrogen iodides into iodine. Since this caused an increase to a value of  $\log (I_0/I) = 0.71$  in the tri-iodide absorption at  $360\mu\mu$ , there must necessarily have been an excess of hydriodic acid present, that is, the concentration of tri-iodide in the solution must have passed through a maximum of type A.

*Effect of the Presence of Hydrogen Peroxide in the Solution.\**—Other experiments, similar to those already described, were carried out, having present in the solution, 2 per cent. (by volume) of a pure 34 per cent. aqueous solution of hydrogen peroxide.

It was found that the presence of the aqueous hydrogen peroxide produced the following effects: (i) the initial rate of formation of the hydrogen tri-iodide band was much accelerated; (ii)  $t_{\max.}$  was much less, that is, the state at which the reactions affecting the ratio  $[I_2]/[HI]$  in opposite senses, balance (corresponding to the attainment of the maximum value for  $[HI_3]$ ) was reached more rapidly; (iii) the absorption curve at this state (that is, at  $t_{\max.}$ ) indicated that the proportion of the iodine present in the form of tri-iodide was much less than that found at the corresponding state (that is, at  $t_{\max.}$ ) for the solution in pure alcohol (curve (b), Fig. 4); and (iv) the extent to which iodine is lost by formation of substitution compounds is much increased.

All four effects are readily explained on the basis of the mechanism which has been put forward.

Presence of water would accelerate reaction (5) with increased initial formation of hydriodic acid and, therefore, of tri-iodide. The hydrogen peroxide will accelerate oxidation of the hydrogen iodides, and thus the fact that all the photochemical reactions have been accelerated should lead to a smaller value for  $t_{\max.}$  effect (iii) merely indicating that reactions (3) and (4) have been accelerated to a greater extent than has reaction (5). Lastly, there is increased formation of acetic acid, and as suggested earlier, iodine will substitute more readily in acetic acid than in acetaldehyde.

### Discussion.

The foregoing results appear to offer an explanation of the discrepancies between observations of previous workers in that their measurements were carried out at varying stages in the formation of hydrogen tri-iodide. It is

\* These experiments are of especial interest in connection with the suggestion made by Schwarzi that pharmaceutical tincture of iodine may be stabilised by addition of hydrogen peroxide.

difficult, however, in connection with the results of Crymble, Stewart and Wright, and of Lowry and Sass, to understand how the tri-iodide band at  $290\mu\mu$  could be recorded and not the satellite band of wave-length  $360\mu\mu$  and of about half the intensity. Apparently, the only possible explanation is that it is usual, in spectrographic measurements, to measure points of low extinctions before those of higher, so that the latter points would be measured at a later stage in the decomposition. Thus, although the maximum at  $290\mu\mu$  was present and measured, yet at the time of taking the earlier measurements at lower extinctions, the decomposition would not have gone so far, so that the tri-iodide absorption at  $360\mu\mu$  was possibly insufficient to show a separate maximum, but only sufficient to cause a distortion of the normal iodine band.

The work which has been described here also provides an explanation of another point, namely, the similarity between the absorption spectra of iodine dissolved in aqueous potassium iodide and in ethyl alcohol. In the former case, the iodine will be present as potassium tri-iodide, whilst, in the latter case, it has been shown to be present as hydrogen tri-iodide, and Winther (*loc. cit.*) has shown that, in aqueous solution, these substances give identical absorption.

### Summary.

(1) The ultra-violet and visible absorption exhibited by solutions of iodine in ethyl alcohol has been investigated.

(2) The maxima recorded by previous workers at  $360\mu\mu$  and  $290\mu\mu$  approximately, in the ultra-violet spectra of such solutions have been proved to be due to formation of hydrogen tri-iodide in the solution, a result in agreement with the suggestion of Stobbe and Schmidt.

(3) Precise measurements of the true absorption curve, between wave-lengths  $250\mu\mu$  and  $720\mu\mu$ , of iodine in alcohol, have been made in the presence of ozone, which decomposes the hydrogen iodides as formed. The curve shows one maximum only, of wave-length  $447\mu\mu$  ( $e_{\max.} = 9.54 \times 10^5$ ) with general absorption in the far ultra-violet.

(4) The hydrogen tri-iodide has been isolated in the solid form upon gelatin, and is shown to exhibit, in this state, an absorption maximum at  $368\mu\mu$ .

(5) The mechanism of the formation of hydrogen tri-iodide has been studied spectrophotometrically. The method devised could be applicable as a general method of use of the sector-photometer, to follow the course of reactions of moderate speed, provided that the absorption changes were of a suitable nature.

(6) It has been shown that, in general, there are, in solutions of iodine in alcohol, opposing reactions—(a) the photochemical reaction between iodine and ethyl alcohol giving hydriodic acid and hydrogen tri-iodide, and (b) the photochemical oxidation of hydrogen iodides by dissolved oxygen. Thus, the absorption curve exhibited will depend on the method and speed of observation, on the light source used, on the purity of the solvent (with regard to its water content), on the dilution of the solution, and on whether the solutions were exposed to daylight, either before or during examination.

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## THE EFFECT OF NITRO-CELLULOSE UPON THE VELOCITY OF CRYSTALLISATION OF GELATIN- ISING SOLVENTS.

BY ANNIE MILICENT KING.\*

(Received, 17th May, 1928.)

The first systematic measurements of linear velocity of crystallisation were obtained by Gernez in 1882.<sup>1</sup> Since then, the study of the velocity of crystallisation of various substances, both in the pure state and in solution, or mixed with other substances, has attracted a large number of investigators. The work described in this paper, however, represents the first measurements of rate of crystallisation of a solvent in which a colloid is dissolved.<sup>†</sup>

In 1921, C. E. Harvey in the University of Bristol laboratory began this study of the rate of crystallisation of 0·2 per cent. solutions of nitro-cellulose in gelatinising solvents which, according to factory experience, range from "very good" to "bad." He found that the extra time taken for crystallisation in the presence of nitrocellulose was exactly parallel to the reputed gelatinising power of the solvent in the six cases investigated. Very good solvents showed an extra time of 0·51 mins. per. cm. of linear crystallisation, and bad solvents only 0·1 mins. Harvey's experiments were confined to this one arbitrary concentration and the solvents used were not specially purified.

The present experiments carried out in 1922 were planned to extend and test Harvey's (unpublished) results by purifying the solvents and by determining the influence of concentration upon the protective action of the nitrocellulose. The investigation, however, was considerably complicated by a phenomenon of polymorphism similar to that which had been observed by Tammann<sup>2</sup> and A. H. R. Muller.<sup>3</sup> Polymorphism seems to be characteristic of the solvents of nitrocotton so far studied. The occurrence of the various forms was largely fortuitous until this was discovered and inoculation was resorted to. It was then found that each form crystallises at a definite rate and obeys Harvey's rule connecting the gelatinising power of various solvents with the protective action exerted upon them by the nitrocellulose.

### Experimental.

**Materials.**—We are much indebted to the staff of Nobel Industries, Ltd., for their invaluable co-operation and for supplying most of the solvents

\* Communicated by Professor J. W. McBain, F.R.S.

<sup>1</sup> *Compt. rend.*, **95**, 1279 (1882).

<sup>†</sup> This work was completed in 1922. The author has since noticed that an article entitled "A Motion-picture Study of the Influence of Gelatin on rates of Crystal Growth and Solution of Copper Sulphate," by W. G. France, has been published in the Third Colloid Symposium Monograph, p. 316.

<sup>2</sup> *Z. physik. Chem.*, **82**, 172-200 (1913).

<sup>3</sup> *Ibid.*, **86**, 177-242 (1914).

used. The nitrocotton used was propulsive soluble nitrocotton washed with acetic acid; ash 0·27 per cent., 12·10 per cent. nitrogen, solubility in alcohol-ether 99·45 per cent., supplied in March, 1919.<sup>4</sup> The solvents were purified by recrystallisation. Special attention was given to the phenyl urethane, several specimens purified in different ways being used.

*Solutions.*—The 0·2 per cent. solutions were prepared by weighing a clean dry tube and adding about 0·02 gms. nitrocotton and weighing again. The calculated amount of solvent was then weighed into the tube, the tube sealed off and placed in a thermostat at 90°. After two hours' shaking, the tube was removed, opened, and the rate of crystallisation measured at different temperatures. Care was taken that the nitrocotton was in fairly small particles before the process of shaking began, since otherwise the solution, instead of being homogeneous after two hours at 90°, contained lumps of clear jelly.

The 2 per cent. solutions took much longer to become homogeneous, ranging from three hours in the case of formanilide to twenty-eight hours for diphenyl urethane, as might be expected from their relative solvent power. After the rate of crystallisation had been measured at various temperatures a weighed amount of solvent was added to the known amount of solution left in the tube and melted in the steam oven. After thorough mixing, the maximum rate of crystallisation of the second solution was measured, and the experiment again repeated with additional solvent so that readings were obtained for maximum crystallisation rate for solutions of various concentrations.

*Method.*—The method consisted in measuring the linear rate of crystallisation of the solution contained in a very clean narrow glass tube, placed in a transparent adjustable thermostat (Fig. 1). A stop-watch reading to a fifth of a second was used in timing the rate. Observations were carried out at various temperatures until the temperature zone of maximum rate, and finally its exact value, had been established.

FIG. 1.



The procedure adopted for the solvents was then applied to the solutions and it was found that the zone of maximum rate corresponds to that of the solvent.

It is impossible to publish at length the mass of data connecting concentration of nitrocotton with rate of crystallisation, which was obtained by this method. Benzophenone, phenyl urethane, diphenyl urethane and (less exhaustively) formanilide, were investigated, and the results compared with data obtained by C. E. Harvey for 0·2 per cent. solutions only of these solvents and of four others, o-tolyl urethane, triphenyl phosphate, ethyl phenyl urethane and benzyl formanilide.

### Benzophenone.

Data obtained for one series of experiments with benzophenone, involving measurements of the rate of crystallisation of the pure solvent at different temperatures are presented in Table I., and are typical of results obtained with other solvents. It will be seen from this table and from Fig. 2, in which temperature is plotted against linear rate of crystallisation in millimetres per second for different solutions of nitrocotton in benzophenone, that the zone of maximum rate is similar for all concentrations of nitrocotton

<sup>4</sup> The same specimen of nitrocotton was used in the experiments communicated by McBain, Harvey, and Smith (*J. Physical Chem.*, **30**, 312 (1926)).

and for the pure solvent. The action of the nitrocotton is simply to reduce

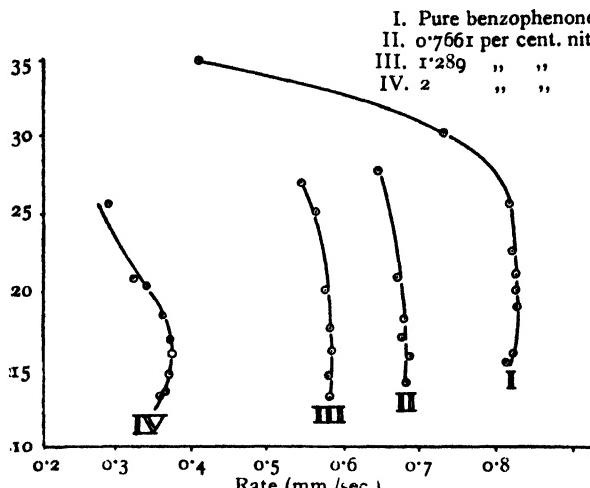


FIG. 2.—Benzophenone.

the rate of crystallisation without otherwise altering or displacing the form of the graph of rate with temperature.

In Fig. 5, which will be discussed in full later, the extra time taken for 1 centimetre of crystallisation is plotted against concentration for each of the substances investigated.

It will be seen that practically a linear relationship is obtained for benzophenone and for the other solvents used.

TABLE I.—RATE OF CRYSTALLISATION OF PURE BENZOPHENONE. EXPERIMENT I.

Temperature. °C.	Distance. Cm.	Time. Mins.	Rate. Mm./sec.	Rate. Mins./cm.
15.1	8.0	1.647	0.8147	0.2046
15.41	8.0	1.629		
16.05	8.0	1.623	0.8251	0.2020
16.08	8.0	1.607		
20.20	8.0	1.612	0.8256	0.2018
20.09	8.0	1.602		
19.07	8.0	1.607	0.8298	0.2009
21.20	7.0	1.407	0.8279	0.2013
21.10	8.0	1.613		
22.95	8.0	1.623	0.8241	0.2022
22.75	8.0	1.613		
25.72	8.0	1.627	0.8218	0.2028
25.78	8.0	1.619		
30.25	6.0	1.379	0.7308	0.2281
30.10	6.0	1.360		
35.20	5.0	2.100	0.4139	0.4027
34.90	6.0	2.320		

Maximum = 0.8298 mm./sec. = 0.2009 mins./cm.

### Diphenyl Urethane.

The phenomena of polymorphism were first prominently met with in the case of diphenyl urethane. Urethane itself is known to exist in at least three forms and the data derived in Tables II. and III. together with Fig. 3, show clearly the existence of these forms which we have labelled  $\alpha$ ,  $\beta$ ,  $\gamma$ .  $\alpha$  being the fastest and  $\gamma$  the slowest in crystallisation. The  $\beta$  form is distinguished by its fibrous appearance, whereas the  $\gamma$  form is a uniform solid mass. The relationships were not clearly understood till the whole of this

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TABLE II.—DIPHENYL URETHANE ALONE. EXPERIMENT I.

Temperature °C.	Remarks.	Rate (mm./sec.).			Rate (mins./cm.).		
		$\alpha$ .	$\beta$ .	$\gamma$ .	$\alpha$ .	$\beta$ .	$\gamma$ .
23·9-23·6	Inoculated.*			0·06247			2·667
25·9-26·0	Inoculated.†			0·06342			2·628
28·9-28·8	Inoculated.†			0·06193			2·690
31·8-32·2	Not inocd.†			0·05832			2·858
36·3-36·3	Not clear.†			0·04943			3·371
33·4	*			0·05691			2·927
12·7-12·5	†	0·1630			1·017		
12·7-12·5	†	0·1604			1·039		
25·6	*		0·1569			1·062	
26·8	*		0·1486			1·121	
16·9	*		0·1485			1·122	
21·5	Inoculated.*		0·1510			1·104	
21·3	†		0·1504			1·108	
23·7	Inoculated.*		0·1519			1·123	
24·8	†		0·1541			1·082	
25·3	†		0·1519			1·123	
28·2	Inocd.† Pt. crystn.			0·06478			2·573
29·9-30·2	Inocd.† Pt. crystn.			0·06498			2·565
16·0-15·9	Pt. crystn.		0·1507			1·106	
13·9-13·6	Pt. crystn.		0·1500			1·111	
22·4-22·1	Inoculated.†		0·1492			1·117	
33·0-32·8	Inoculated.*			0·05952			2·800
25·1-24·8	Inoculated.*†		0·1518			1·098	

\* Uniform solid mass.

† Fibres.

Mean (up to 25·3°) = 0·1510 mm./sec. = 1·104 mins./cm. ( $\beta$  form).Mean (up to 31·0°) = 0·06352 mm./sec. = 2·624 mins./cm. ( $\gamma$  form).

TABLE III.—0·2 PER CENT. NITROCOTTON IN DIPHENYL URETHANE.

Temperature. °C.	Remarks.	Rate (mm./sec.).		Rate (mins./cm.).	
		$\beta$ .	$\gamma$ .	$\beta$ .	$\gamma$ .
26·1-26·4	*			0·06250	
20·8-20·6	*			0·06243	
23·0-23·1	*			0·06309	
31·1-31·0	*			0·06668	
36·8-36·7	*			0·05048	
41·9-41·8	*			0·03714	
15·5	†	0·1415			1·178
15·5	* †			0·06361	
24·4-24·2				0·06117	
35·2	Not clear			0·06043	
15·0-15·2	†	0·1407			1·184
17·6-17·8	†	0·1394			1·195
17·6-17·4	†	0·1408			1·184
22·2-22·2	†	0·1429			1·166
25·7-25·7	†	0·1409			1·183
29·5	†	0·1410			1·182
24·3-24·4	†	0·1429			1·166

\* Uniform solid mass.

† Fibres.

Mean (up to 25·0°) = 0·1414 mm./sec. = 1·179 mins./cm. ( $\beta$ ).Mean (up to 31·5°) = 0·0625 mm./sec. = 2·677 mins./cm. ( $\gamma$ ).Note.—From one experiment, the rate of crystallisation of the  $\alpha$  form at 22·1° = 0·1581 mm./sec. = 1·054 mins./cm.

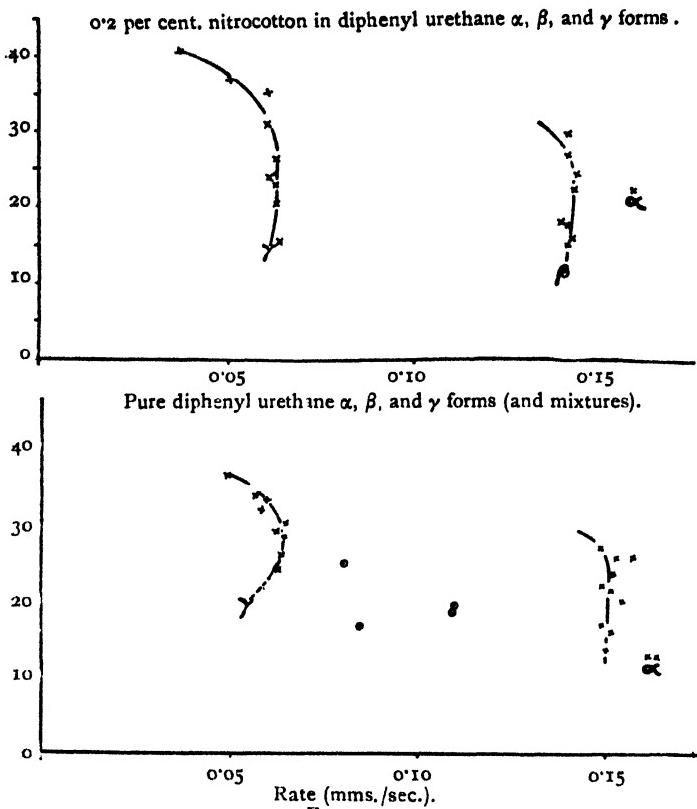


FIG. 3.

TABLE IV.—DIPHENYL URETHANE ALONE (A STILL PURER SPECIMEN).  
EXPERIMENT II.

Temperature. °C.	Rate (mm./sec.).		Rate (mins./cm.).	
	$\alpha$ .	$\beta$ .	$\alpha$ .	$\beta$ .
+28·0		0·1515		1·110
+28·2		0·1510		1·104
+31·1		0·1528		1·091
+36·2-36·1		0·1520		1·094
+44·4-44·1	0·1544		1·080	
*19·8	0·1683		0·9924	
+25·6	0·1807		0·9224	
+25·7	0·1777		0·9378	
+29·5	0·1742		0·9566	
+29·35	0·1602		1·040	
+54·1	0·1196		1·393	
+46·5	0·1570		1·061	
+38·5		0·1551		1·074
+25·5		0·1481		1·125

\* Uniform solid mass.

† Fibres.

Mean ( $\beta$  form) = 0·1518 mm./sec. = 1·098 mins./cm.Mean ( $\alpha$  form) = 0·1722 mm./sec. = 0·9681 mins./cm.

Note.—At five temperatures between 16·1° and 25·8°, point crystallisation was obtained

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work had been completed but the interpretation is confirmed by the data for the more concentrated solutions presented in Tables IV., V., VI., and VII., which are analysed in Fig. 4. The data refer almost entirely to the

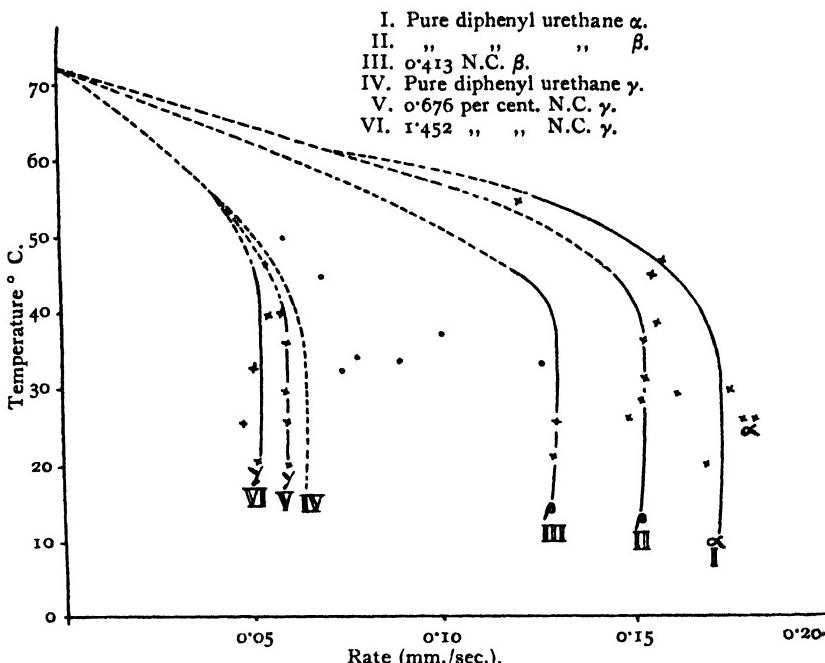


FIG. 4.—Diphenyl urethane  $\alpha$ ,  $\beta$  and  $\gamma$  forms.

TABLE V.—RATE OF CRYSTALLISATION OF 1.45 PER CENT. SOLUTION OF NITRO-COTTON IN DIPHENYL URETHANE.

Temperature °C.	Inoculated (?)	Form.	Rate (mm./sec.)	Rate (mins./cm.)
20.60	Spontaneous	$\gamma$	0.05175	3.220
25.45-25.15	"	$\gamma$	0.04704	3.542
39.70	Inoculated	$\gamma$	0.05430	3.069
45.50	"	$\gamma$	0.05337	3.122
29.60-29.90	Spontaneous	$\gamma$	0.05830	2.858
34.85	Inoculated	$\gamma$	0.05038	3.308

$$\text{Mean up to } 40^\circ = 0.05236 \text{ mm./sec.} = 3.183 \text{ mins./cm. } (\gamma \text{ form}).$$

TABLE VI.—RATE OF CRYSTALLISATION OF 0.676 PER CENT. NITROCOTTON IN DIPHENYL URETHANE.

Temperature. °C.	Inoculated (?)	Form.	Rate (mm./sec.)	Rate (mins./cm.)
20.00	Inoculated	$\gamma$	0.05940	2.805
25.45-25.00	"	$\gamma$	0.05897	2.826
29.85-29.65	"	$\gamma$	0.05925	2.812
35.90-35.80	"	$\gamma$	0.05920	2.815
40.15-39.90	"	$\gamma$	0.05732	2.907

$$\text{Mean (up to } 36^\circ) = 0.05920 \text{ mm./sec.} = 2.815 \text{ mins./cm. } (\gamma \text{ form}).$$

TABLE VII.—RATE OF CRYSTALLISATION OF 0·4126 PER CENT. NITROCOTTON IN DIPHENYL URETHANE.

Temperature °C.	Inoculated (?)	Form.	Rate (mm./sec.)	Rate (mins./cm.)
21·05-21·00	Spontaneous	$\beta$	0·1278	1·305
25·20	"	$\beta$	0·1290	1·292
30·75	"	$\beta$	0·1282	1·300
36·40-36·50	"	$\beta$	0·1282	1·300
41·75	"	$\beta$	0·1272	1·310

Mean (up to 36·5) = 0·1283 mm./sec. = 1·299 mins./cm. ( $\beta$  form).

$\beta$  and  $\gamma$  forms, with a few odd results corresponding to  $\alpha$  form. Bakr in this laboratory in 1919 obtained results which although carried out at 55°, agree well with the present explanation, leading to an almost identical value for protective action on the  $\gamma$  form.

It should be noted that inoculation is a necessary, though often unsuccessful expedient, in attempting to procure crystallisation in any one form of diphenyl urethane.

The spontaneous formation of crystals from point sources in the body of the liquid became so frequent at lower temperatures that the measurement of the linear rate of crystallisation was completely interfered with, and the study was only carried down to the region of maximum rate.

### Phenyl Urethane.

The data for diphenyl urethane have been described in detail, since they are characteristic of results obtained with solvents showing polymorphism. Phenyl urethane was very similar in behaviour to diphenyl urethane. The results obtained are briefly presented in the summary Table VIII.

Phenyl urethane proved to be particularly puzzling, but carefully purified samples of the solvent gave a definite result, Harvey's values agreeing closely with those of the writer.

Here again there are three forms,  $\alpha$ ,  $\beta$  and  $\gamma$ , the quickest of which,  $\alpha$ , was not readily isolated. Its erratic appearance suggested at first sight that in some cases nitrocotton was having an accelerating effect upon the crystallisation of the solvent, a result which would have been at variance with all presuppositions. The final interpretation brings into line all of the observed results and confirms the unpublished work of Bakr in 1919.

### Triphenyl Phosphate.

A few experiments with triphenyl phosphate were carried out by Harvey, and seemed to point to the existence of two forms,  $\alpha$  and  $\beta$ , having rates of crystallisation of 1·60 and 1·67 mins./cm. respectively. These results are summarised in Table VIII. which also contains data obtained by him with ethyl phenyl and o-tolyl urethanes and benzyl formanilide which were studied in concentrations of 0·2 per cent. only.

### Formanilide.

0·2 per cent. solutions of nitrocotton in formanilide were studied by Harvey, and gave two forms  $\alpha$  and  $\beta$ , having extra times of 0·18 and 0·50 mins./cm. of crystallisation. When the writer attempted to extend the study to more concentrated solutions, fluctuating results were obtained which

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TABLE VIII.—PROTECTIVE ACTION OF NITROCOTTON UPON THE MAXIMUM RATE OF CRYSTALLISATION OF VARIOUS SOLVENTS; EXPRESSED IN MINUTES REQUIRED FOR 1 CM. OF CRYSTALLISATION.

Solvent.	Solution.	T <sub>solv.</sub> Mins.	T <sub>solv.</sub> Mins.	T <sub>solv.</sub> — T <sub>solv.</sub> Mins.	T <sub>solv.</sub> — T <sub>solv.</sub> 0·2 Per Cent.	Reputation.
Benzophenone	2·00	0·44	0·20			
	2·00	0·42	0·20	0·22	0·02	
	1·29	0·28	0·20	0·08	0·01	
	1·14	0·28	0·20	0·08	0·02	
	0·77	0·24	0·20	0·04	0·01	
	0·62	0·24	0·20	0·04	0·01	Mean = 0·015
Diphenyl urethane	C.E.H. 0·20	0·215	0·203			
	1·45 γ	3·18	2·62	0·56	0·07	
	0·68 γ	2·82	2·62	0·20	0·06	
	0·41 β	1·30	1·10	0·20	0·10	
	0·20 γ	2·68	2·62	0·06	0·06	
	β	1·18	1·10	0·08	0·08	Mean = 0·06 (γ), 0·09 (β)
Phenyl ure- thane	2·08 γ	6·15	4·94 (C.H.)	1·21	0·12	Poor
	1·72 γ	5·91	4·94 "	0·97	0·11	
	1·25 γ	5·85	4·94 "	0·91	0·15	
	0·69 γ	5·59	4·94 "	0·65	0·19	
	0·20 γ	4·94	4·94 "	(0·00)		
	C.H. 0·20 γ	4·89	4·94 "	(- 0·05)		
	C.H. 0·10 γ	4·94	4·94 "	(0·00)		
	2·22 γ	6·15	4·94 "	1·21	0·11	
	1·38 γ	5·73	4·94 "	0·89	0·13	
	0·91 γ	5·55	4·94 "	0·61	0·13	
	0·50 γ	5·52	4·94 "	0·58	0·13	
	0·66 γ	5·47	4·94 "	0·53	0·16	
	0·53 γ	5·13	4·94 "	0·19	0·07	
	0·46 γ	5·28	4·94 "	0·34	0·15	
	0·40 γ	5·22	4·94 "	0·28	0·14	
	0·23 γ	5·10	4·94 "	0·16	0·14	
	0·45 γ	4·45	4·12	0·33	(0·15)	
	0·35 β	4·20	4·12	0·08	0·05	
	0·34 β	3·80	4·12	- 0·32	—	
	0·18 β	4·14	4·12	0·02	0·02	
	0·14 β	4·22	4·12	0·10	0·01	
	0·30 β	3·92	4·12	- 0·20	—	
	0·21 β	3·78	4·12	- 0·34	—	Mean = 0·13 (γ), 0·06 (β)
	0·20 β	4·12	4·12	0·00	—	
Triphenyl phosphate (C.H.).	0·20	1·74	1·67	0·07 β		Unknown, concluded only fair
			1·60	0·14 α		
Formanilide	2·00	11·16	9·82			
	2·00	10·72	9·82	(1·34) (0·90)	(0·13) (0·09)	
	1·23	10·44	9·82	(0·62)	(0·10)	
	0·87	10·35	9·82	(0·53)	(0·12)	
	0·80	10·34	9·82	(0·52)	(0·13)	
	0·33	10·12	9·82	(0·30)	(0·18)	
	(C.H.) 0·20 α	10·10	9·92	(0·18)		
	β	10·42	9·92	(0·50)		
	0·20	1·53	1·44	0·09	0·09	Fair
O-tolyl ure- thane (C.H.).	0·20	4·39	3·88	0·51	0·51	Very good
Ethyl phenyl urethane (C.H.).	0·20	2·09	1·81	0·28	0·28	Good
Benzyl for- manilide (C.H.).						

possess little significance since almost certainly several modifications are concerned.

### Discussion.

When the data for the effect of concentration of nitrocotton collected in Fig. 5 are considered, it is seen that the relation between protective action and concentration of nitrocotton is simply linear.

The same figure and Table VIII presents all the results here obtained for comparison with our rule. In the last column of the table the protective action recorded is referred to a 0·2 per cent. solution so as to make that result comparable with previous work. The last column gives the reputed solvent power. It is seen that on the whole our rule, that the extra time taken for crystallisation in presence of nitrocotton is exactly parallel to the reputed gelatinising power of the solvent, is obeyed. The case of triphenyl phosphate

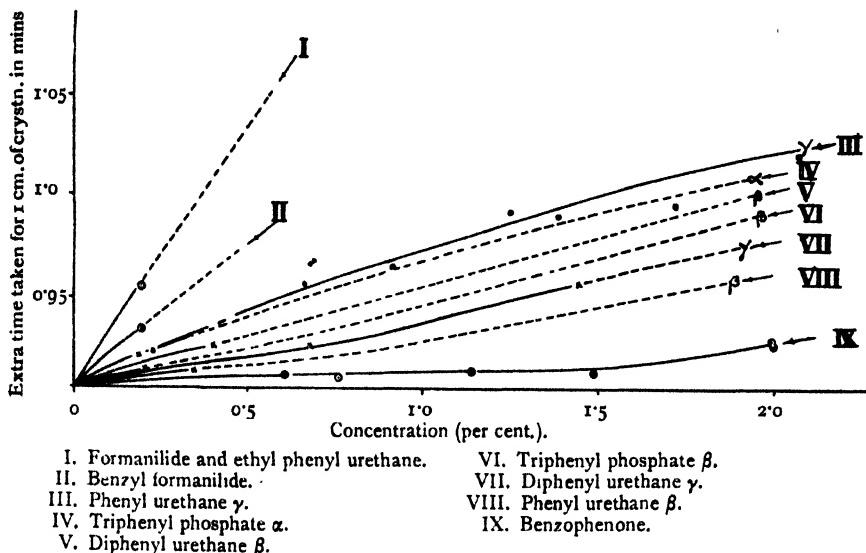


FIG. 5.—Extra time/concentration.

is interesting as no information as to its solvent power was available at the time. It appears to be only a fair gelatiniser. The same result was obtained by the viscosity method, which has hitherto been the only thoroughly satisfactory and rapid method for testing gelatinising power. However, the method of crystallisation here described may be useful in particular cases, as is illustrated by these results with triphenyl phosphate.

A theoretical definition connecting solvent power with viscosity is given by McBain, Harvey and Smith.<sup>5</sup> "The apparent viscosity of the solutions is almost entirely due to the presence of loose ramifying aggregates of colloidal particles united by local and specific bonds of residual affinity of different kinds and degree. The best solvents are those which most effectively combine with these bonds and by themselves satisfying the residual affinities dismember the aggregates. Hence, the best solvents yield solutions of the lowest apparent viscosities. A technical definition of solvent power may be based upon the uniform appearance and ease of pressing of nitrocotton gelatinised under manufacturing conditions, but this

<sup>5</sup> *J. Physical Chem.*, 30, p. 352, 1925.

is not quite the same as the insistence that the solvent itself in sufficient quantity produces a fluid sol."

From Table VIII., on comparing Harvey's results with those of the writer, the protective action of the nitrocotton appears to be very much the same even when small amounts of impurity are present.

We have therefore shown that the gelatinising power of a solvent is parallel to the extra time taken for that solvent to crystallise in the presence of nitrocotton. Close investigation is, however, necessary on account of the possible complications introduced by the frequent appearance of the property of polymorphism in the crystals.

### **Summary.**

1. The linear rate of crystallisation of the following solvents has been measured, together with that of solutions of different nitrocotton concentration in their zone of maximum rate: benzophenone, diphenyl urethane, phenyl urethane, triphenyl phosphate, formanilide.<sup>6</sup> Ethyl phenyl urethane, and o-tolyl urethane have been investigated in 0·2 per cent. nitrocotton solution.

2. Diphenyl urethane appears in three crystalline forms,  $\alpha$ ,  $\beta$ ,  $\gamma$ , the  $\beta$  form having an extra time of 0·09 minutes per cm. for 0·2 per cent. nitrocotton, and the  $\gamma$  form an extra time of 0·06 minutes.

3. Phenyl urethane appears in at least two forms,  $\beta$  and  $\gamma$ , the  $\beta$  form having an extra time of 0·06 minutes per cm. for 0·2 per cent. nitrocotton, and  $\gamma$  form an extra 0·13 minutes.

4. Triphenyl phosphate appears in two forms  $\alpha$  and  $\beta$ , the  $\alpha$  form having an extra time of 0·14 minutes for 0·2 per cent. nitrocotton and the  $\beta$  form an extra time of 0·07 minutes.

5. Formanilide appears in two forms, the slower of which takes an extra time of 0·51 minutes for 0·2 per cent. nitrocotton.

6. In accordance with unpublished work of Dr. C. E. Harvey the extra time taken for crystallisation goes parallel with the solvent power of all the solvents used. Presumably this is due to more vigorous and extensive solvation of the nitrocotton by the best solvents.

This study was undertaken at the suggestion of Professor J. W. McBain, F.R.S., to whom I am indebted for his constant interest and friendly advice.

<sup>6</sup> It is found that in almost every case several solid modifications of crystallisation may appear. In each case, however, the nitrocotton has a retarding effect upon the rate of crystallisation of the solvent and the extra time required is approximately proportional to the amount of nitrocotton present.

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# THE INFLUENCE OF LYOPHILE COLLOIDS ON THE PRECIPITATION OF SALTS. AGAR-AGAR AND LEAD IODIDE.

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Previous investigations<sup>1, 2, 3</sup> have shown that under appropriate conditions gelatin is able to prevent the formation of solid silver chromate by the interaction of silver nitrate with potassium chromate, though the concentrations of these substances may be far in excess of those corresponding to the solubility product of silver chromate. Further, a relatively large proportion of the silver is found to remain in the form of simple ions.<sup>3</sup> From several points of view it is of importance to ascertain whether this state of affairs is peculiar to a particular system. The influence of agar-agar on the formation of lead iodide by the addition of potassium iodide to lead nitrate was therefore investigated.

The choice of the system agar-lead iodide was made for various reasons. In the first place there is the difference in chemical nature between agar (carbohydrate) and gelatin (protein). Then the system has been studied in connection with periodic precipitation.<sup>4</sup> Also the crystallisation of lead iodide from aqueous solution in the absence of colloid has been the object of special attention.<sup>5</sup> Finally, the possibility exists of determining, by electromotive force measurements, the actual concentrations of both the lead and iodide ions in mixtures of agar, lead nitrate, and potassium iodide.

## Precipitation Experiments.

A commercial powdered agar-agar was used, which yielded 17·60 per cent. moisture when dried at 105° C. and gave 4·0 per cent. (calculated on dry material) of ash. The latter contained large amounts of calcium sulphate. Estimated by the Kjeldahl method, the nitrogen content of the agar was found to be 0·45 per cent. (calculated on dry material). Comparison with the results of analyses recorded by various workers,<sup>6</sup> shows that the agar was a normal product. It was not subjected to any process of purification.

Several lots of lead nitrate, recrystallised twice from water, and two samples of potassium iodide, one A.R., were employed in making up the salt solutions. The conductivity measurements described below indicated that these materials were sufficiently pure.

The following procedure was adopted. One gram of agar (undried) was dispersed in 50 c.c. conductivity water by heating for one hour on the

<sup>1</sup> Williams and Mackenzie, *J. Chem. Soc.*, 117 (1920), 844.

<sup>2</sup> Bolam and Mackenzie, *Trans. Faraday Soc.*, 22 (1926), 151, 162.

<sup>3</sup> Bolam and Desai, *Ibid.*, 24 (1928), 50.

<sup>4</sup> Hatschek, *Koll. Z.*, 10 (1912), 124; 14 (1914), 115. Chatterji and Dhar, *Koll. Z.*, 40 (1926), 97.

<sup>5</sup> Volmer, *Z. physik. Chem.*, 102 (1922), 267. Notboom, *Koll. Z.*, 32 (1923), 247. Fischer, *Z. anorg. Chem.*, 145 (1925), 311.

<sup>6</sup> Fellers, *J. Ind. Eng. Chem.*, 8 (1916), 1128. Fairbrother and Mastin, *J. Chem. Soc.*, 123 (1923), 1412.

## THE PRECIPITATION OF SALTS

steam bath, in a flask fitted with a ground-in water-cooled reflux condenser. Equal volumes of suitable equivalent solutions (in conductivity water) of lead nitrate and potassium iodide were now added, the whole well mixed, and about 20 c.c. of the mixture poured into a glass tube. This was immediately corked and placed in a 25° C. thermostat, the agar mixture being protected against any action of the light. All the glass-ware used was thoroughly cleaned with chromic acid and steamed-out (for some hours in case of flask).

Each experiment was duplicated and the results are given in Table I., where  $C$  = concentration of lead nitrate and of potassium iodide (after mixing) in milli-equivalents per 1000 grams water. It was found that about 0·4 gram of water was lost by evaporation from the hot agar during the mixing operations and this has been allowed for in calculating  $C$ . The concentration of the agar is given as grams dry agar per 100 grams water. The third column of the table gives the time interval between placing the tube in the thermostat and making the observation.

TABLE I.

$C.$	Agar Per Cent.	Time.	Observations
3·173	1·239	72 hours.	No change.
3·313	1·239	48 "	" "
7·911	1·239	72 "	" "
10·26	1·239	24 "	Slight change, if any.
		48 "	Small number of spherolites.
		72 "	16-20 small spherolites.
10·89	1·239	18 "	Many more spherolites. Earlier ones had increased in size.
		42 "	Mixture pale yellow when prepared.
12·62	1·239	0 mins.	Abundant yellow precipitate in all parts of gel.
9·722	1·334	48 hours.	No change.
10·67	1·303	72 "	Traces of precipitate on side tube.
		24 "	Slight change, if any.
		40 "	Small amount precipitation; traces of yellow colour or very few spherolites.
11·58	1·273	12 "	Pale yellow throughout.
		24 "	Large number very small spherolites. Gel stronger yellow.

Except at the salt concentrations 12·62 and 11·58, the bulk of the gel did not show any yellow colour. The "spherolites" (spherical aggregates)

TABLE II.

$C.$	Observations.
3·173	No precipitation after 40 hours.
3·313	" " " 24 "
3·821	" " " 48 "
4·008	Very small amount precipitation after 24 hours.
5·010	Precipitation commenced before temp. reached 25° C. A large amount of precipitate had appeared after 24 hours.

were orange in colour. Their formation has been observed by Hatschek<sup>7</sup> in the case of lead iodide in agar, and in many other instances.

<sup>7</sup> *J. Soc. Chem. Ind.*, 30 (1911), 255.

The precipitation of  $\text{PbI}_2$  by the same reaction in the absence of agar was now studied. Equal volumes of equivalent solutions of  $\text{Pb}(\text{NO}_3)_2$  and  $\text{KI}$  were mixed at a temperature sufficiently high to prevent precipitation. The mixtures were then kept at  $25^\circ\text{C}$ . The observations are recorded in Table II., each experiment being carried out at least in duplicate.

Comparison of the two tables leads to the conclusion that the presence of agar opposes to a marked degree the precipitation of lead iodide. For example, immediate precipitation occurred at  $C = 5.010$  in the absence of agar, whereas in the presence of  $1.239$  per cent. of the latter only a small amount of lead iodide was visible when  $C = 10.26$ , even after 72 hours.

### Conductivity Determinations.

To obtain information concerning the nature of the action of the agar, measurements were made of the conductivities of various systems. The ordinary method was employed, a calibrated three metre Kohlrausch Wheel bridge, a Class B Gambrell resistance box (accurate to 1 in 1000), and conductivity cells of the Ostwald type, being used. The cell constants were frequently checked. To carry out a determination the hot agar mixture was poured into a clean and dry cell, the electrodes, dried with absolute alcohol, inserted and moved up and down to displace air bubbles, and the cell placed immediately in the thermostat. The agar was found to set within five minutes.

In Tables III. and IV. are given the conductivities of the mixtures of lead nitrate, potassium iodide, and agar ( $K_1$ ), together with those of mixtures of agar and potassium nitrate at the same concentrations as in the iodide mixtures ( $K_2$ ). Each mixture was kept in the thermostat for 24 hours and the conductivity determined from time to time. For the actual measurements the temperature was brought to  $25.08 \pm 0.01^\circ$  (corrected); otherwise it was kept within a few tenths of  $25^\circ$ .

TABLE III.

C.	Agar Per Cent.	$K_1$ (Specific cond. $\times 10^6$ )			$K_2$ (Specific cond. $\times 10^6$ )			$K_1 - K_2$
		Mean.		Mean.				
3.173	1.239	1102 1102 1105	1103	794 796 800	797		306	
3.313	"	1126 1124	1125	815 821 818	817		308	
7.911	"	2106 2113	2109	1411 1402	1406		703	
10.26	"	2594 2581	2588	1704 1702	1703		885	
9.722	1.334	2487 2487	2487	1652 1640	1646		841	
10.67	1.303	2671 2681	2676	1778 1760	1769		907	

In all the conductivity work at least two quite independent experiments were made for each concentration. The individual results, together with

## THE PRECIPITATION OF SALTS

mean values, are given in the tables and show the degree of reproducibility attained. All values have been corrected for the conductivity of the water ( $1 - 2 \times 10^{-6}$ ).

The values of  $K_1$  for the mixtures in Table III. were almost constant for 24 hours. They were generally found to be slightly decreasing from the time of the first reading (about 40 mins.) until some hours later (up to 12) when they became constant within 0.1 per cent. The decrease averaged about 0.4 per cent. and the final constant values of  $K_1$  are given above.

TABLE IV.

C.	Agar Per Cent.	Time.	$K_1$ .	$K_2$	$K_1 - K_2$	Decrease.
10.89	1.237	40 mins. 23 hours	2730 2701	1784 "	946 917	29
"	"	40 mins. 24 hours	2737 2667	" "	953 883	70
12.62	"	36 mins. 4 hours	2883 2733	1998 "	885 735	150
"	"	36 mins. 25 hours	2815 2692	" "	817 684	133
11.58	1.273	2 hours 24 "	2822 2697	1879 "	943 818	125
"	"	2 hours 24 "	2810 2707	" "	931 824	107

TABLE V.

C.	Time.	Specific Conductivity, (Pb(NO <sub>3</sub> ) <sub>2</sub> + KI) × 10 <sup>-6</sup>	Specific Condv. KNO <sub>3</sub> × 10 <sup>6</sup>	Difference.
<i>Mean.</i>				
3.173	—	824 822 825	824	442
3.313	—	859 858	859	462
3.821	—	975 979 977 978	978	531
4.008	40 mins. " 24 hours " "	1026 1024 1025 1028	1026	556
5.010	23 mins. 39 " 24 hours " " " " " , *	1205 1189 1122 1154 1128 1116.5 1120.3	692 " " " " " "	513 497 430 462 436 424.5 428.3

The conductivities at the same temperature of mixtures of  $\text{Pb}(\text{NO}_3)_2$  and KI in the absence of agar were also determined and will be found in Table V. The fourth column of the latter contains the conductivities of the corresponding concentrations of  $\text{KNO}_3$ . A cell with vertical electrodes and closed with a glass stopper was used for these determinations. In the case of the first three concentrations, the mixture was placed in the cell immediately after preparation and the conductivity determined from time to time. It was found to remain constant within 0.1 per cent for 24 hours. At the two higher concentrations the conductivity was either determined immediately or else after the mixture had been kept at  $25 \pm 0.1^\circ$  for 24 hours in a Duroglass resistance glass bottle. In the two experiments marked with \* the latter was kept revolving the whole time, to make the crystallisation as complete as possible.

It was necessary to know the conductivities of mixtures of agar and individual salts at  $25.08^\circ$ . Mixtures were prepared and their conductivities found in exactly the same way as for the lead iodide-agar systems. The results are shown in Table VI., along with the conductivity of the agar itself and the conductivities of the salts in the absence of the latter. The last column of the table gives the differences between the conductivity of the mixture (agar + salt) and the sum of the separate conductivities of the agar and the salt.

TABLE VI.

Salt.	C.	Specific Condy. (Agar + Salt $\times 10^6$ ). (a).	(Specific Condy. $1.239$ Per Cent. Agar $\times 10^6$ ). (b).	(Specific Condy. Aq. Salt $\times 10^6$ ). (c).	$b + c$ .	Difference ( $b + c - a$ ).
$\text{KNO}_3$	3.173	798	386	432*	828	30
	3.313	817	"	462	848	31
	7.911	1406	"	1084	1470	64
	12.62	1998	"	1698	2084	86
$\text{Pb}(\text{NO}_3)_2$	<i>Mean</i>					
	3.173	673	674	408 <sup>a</sup>	794	120
	7.911	1159	1155	969	1355	200
	12.62	1619	1619	1489	1875	256
KI	3.173	817	817	462 <sup>10</sup>	848	31
	7.911	1449	1452	1129	1515	63
	12.62	2058	2068	1779	2165	97
		2079				

The figures for the salt solutions (fifth column) were compared with those obtained by the workers indicated and found to be in good agreement. The conductivity of the agar itself or of a mixture with any single

<sup>a</sup> Ostwald, *Z. physikal. Chem.*, I (1893), 74.

Kohlrausch und Grüneisen, *Berl. Sitz. ber.* (1904), 1215.

<sup>10</sup> Bray and Mackay, *J. Amer. Chem. Soc.*, 32 (1910), 914.

salt was found in 24 hours to decrease in the same way and to the same extent as the conductivity of the lead iodide-agar mixtures in Table III.

### Saturated Lead Iodide.

Lead iodide was prepared by mixing equal volumes of  $N/10$  lead nitrate and  $N/10$  potassium iodide, washing the precipitate thoroughly and drying slowly in the dark. About 0.5 gm. was rotated with approximately 200 c.c. conductivity water in a carefully cleaned resistance glass bottle for over 24 hours at  $25 \pm 0.1^\circ$  (corrected), light being excluded. The solution was then forced by air pressure through a hardened filter paper (first few c.c.s rejected) and its conductivity determined at  $25.08^\circ$ . Five independent experiments gave the mean value 426.8 (428.0, 425.2, 429.4, 425.1, 426.4). In the case of the first two the lead iodide was recrystallised twice from water and carefully dried. Converting to Siemen's units we obtain 401 as the conductivity of saturated lead iodide at  $25^\circ$ , in good agreement with the results of Noyes and Woodworth<sup>11</sup> who found 402.1 working from under saturation and 404.1 from supersaturation.

Denham,<sup>12</sup> on the other hand, considers that 472.2 is the true value and maintains that lower values are due to atmospheric oxidation of the lead iodide. The experiments recorded in Table V., however, suggest strongly that Denham was dealing with a supersaturated solution. It will be seen that the conductivity of  $4.008 \times 10^{-3}$  equivalent  $\text{Pb}(\text{NO}_3)_2$  per 1000 grams / +  $4.008 \times 10^{-3}$  equivalent KI per 1000 grams or of a less concentrated mixture is constant for 24 hours, whereas at the concentration  $5.010 \times 10^{-3}$  equivalents per 1000 grams the conductivity gradually decreases. Further, the values given in the last column of the table, which represent approximately (see below) the conductivity of the lead iodide, support the view that supersaturation takes place. Moreover, while precipitation occurs only to a very small extent at the lower concentration it is immediate and abundant at the higher (Table II.).

To test the matter further, in the last two of the above mentioned experiments the saturated solution was collected in two portions, one of which was used for the conductivity determination, while the other was weighed and the lead precipitated as lead chromate. The solution was heated, acidified with acetic acid, excess of potassium chromate added, and the whole well stirred to ensure coagulation of the very fine precipitate.

After cooling, the precipitate was filtered through a Gooch crucible, well washed, and dried at  $120^\circ$  to constant weight. In this way the solubility of lead iodide at  $25^\circ$  was found to be 1.645 millinols per 1000 grams water (both determinations gave exactly the same figure) which agrees closely with the values of Lichtry<sup>13</sup> (1.65), and Lewis and Brighton<sup>14</sup> (1.65).

The values of the conductivity of the lead iodide formed at the various concentrations of lead nitrate and potassium iodide will actually be somewhat greater than the values shown in the last column of Table V. In obtaining these latter it has been assumed that all the nitrate is in the form of potassium nitrate, thereby neglecting the appreciable quantity of undisassociated lead nitrate present. Some idea of the error involved was obtained by the following experiment. Saturated lead iodide solution was prepared at  $25^\circ$  from the solid in the manner described above. One weighed portion

<sup>11</sup> Noyes and Woodworth, *Z. physikal. Chem.*, **26** (1898), 152.

<sup>12</sup> Denham, *J. Chem. Soc.*, **III** (1917), 39.

<sup>13</sup> Lichtry, *J. Amer. Chem. Soc.*, **25** (1903), 467.

<sup>14</sup> Lewis and Brighton, *Ibid.*, **39** (1917), 1906.

was diluted with water to give 2.888 milli-equiv./1000 grams and a second with potassium nitrate solution to give the same concentration of  $\text{PbI}_2 + 0.01219 N \text{KNO}_3$ . The conductivity of the lead iodide at 25° was found to be 375.7, that of potassium nitrate 1640.3; sum = 2016.0. On the other hand the conductivity of the mixture was 1968.8, a difference of 47.2.

### Discussion.

Attention should be in the first place directed to the figures in the last column of Table III. ( $K_1 - K_2$ ). If e.g. in the presence of 1.239 per cent. agar in every case the reaction  $(\text{Pb}(\text{NO}_3)_2 + \text{KI} \rightarrow \text{PbI}_2 + 2\text{KNO}_3)$  proceeded to completion, i.e. if lead iodide was precipitated until the solution was just saturated, the value of  $K_1 - K_2$  should be 308 or less. Instead of this it can be almost three times as great, as when  $C = 10.26$ . Moreover in these particular mixtures the value of  $K_1 - K_2$  remains practically constant for 24 hours and there is either no sign of precipitation or very little for 48 hours or more (Table I.). On the other hand comparison of Tables I. and IV. shows that at higher salt concentrations where precipitation is visibly proceeding, the value of  $K_1 - K_2$ , while high, gradually but unmistakably decreases. In 24 hours it may fall below the values obtained with the less concentrated mixtures.

These facts are in harmony with the view that the lead iodide in those mixtures which show a constant value for the conductivity, exists largely in the form of free ions. That is to say, the agar maintains the lead iodide in supersaturated solution and prevents the formation of solid lead iodide. If this is the case, supersaturation in the presence of agar obviously persists to much higher concentrations than in its absence. It should be pointed out that, assuming supersaturation, the conductivity of the lead iodide will actually be greater than  $K_1 - K_2$  (Table III.), as explained in the last section.

It necessarily follows from the foregoing that the lead iodide cannot be in the colloidal condition.\* This is borne out by the fact that the mixtures in question have exactly the same appearance as agar + lead nitrate. There is no colour change such as would be expected from the formation of a sol of  $\text{PbI}_2$ .

The question arises of how much change does take place when lead nitrate and potassium iodide are brought together in the presence of agar. Some information with regard to this point may be obtained by comparing, for a given concentration, the value of

$$[\text{Cond.} (\text{Agar} + \text{Pb}(\text{NO}_3)_2) + \text{Cond}(\text{Agar} + \text{KI})]$$

with that of

$$[\text{Cond}(\text{Agar} + \text{Pb}(\text{NO}_3)_2 + \text{KI}) + \text{Cond. Aga}]r,$$

using the data in Tables III. and VI. When  $C = 3.173$ , we have  $674 + 817 = 1491$ , and  $1103 + 386 = 1489$ . For  $C = 7.911$ , however, we have  $1155 + 1452 = 2607$ , as compared with  $2109 + 386 = 2495$ , giving the considerable difference of 112. Such a change was always found to happen with silver nitrate, potassium chromate, and gelatin.<sup>2</sup> At present its significance is not clear.

It will be observed from Table VI. that the conductivity of a mixture of agar and salt is always less than the sum of their separate conductivities.<sup>13</sup>

\* Cf. Chatterji and Dhar, *loc. cit.*

<sup>13</sup> Iwase, *Bull. Chem. Soc. Jap.*, 2 (1927), 61, found the same behaviour.

While, however, the difference is only about 4 per cent. in the case of  $\text{KNO}_3$  or  $\text{KI}$ , it is very much more for  $\text{Pb}(\text{NO}_3)_2$ . The explanation of this is probably as follows: The addition of potassium iodide or nitrate to the agar produced no visible change, but lead nitrate gave rise to an unmistakable increase in turbidity. There is a good deal of evidence<sup>16</sup> that agar-agar consists principally of the calcium salt of an acid sulphuric ester ( $\text{Ca}(\text{O} \cdot \text{SO}_2 \cdot \text{O} \cdot \text{R})_2$ ) which hydrolyses on heating to give sulphuric acid. The turbidity produced as above will thus be lead sulphate, the formation of which accounts for the relatively large decrease in conductivity.

The influence of agar on the precipitation of lead iodide resembles that of gelatin on the formation of silver chromate. Discussion of the exact nature of this influence is reserved until the electrometric investigation in progress has been completed.

The author's thanks are due to Sir James Walker for his interest and support, to the Carnegie Trust for the grant of a Teaching Fellowship, and to Messrs. Brunner, Mond & Co., and the Earl of Moray Research Fund for assistance in obtaining apparatus and materials.

<sup>16</sup> Fairbrother and Mastin, *loc. cit.*; Hoffmann and Gortner, *J. Biol. Chem.*, **65**, (1925), 371; Samec and Ssajevic, *Koll. Chem. Bih.*, **16** (1922), 285.

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## THE INITIATION OF FLAME IN MIXTURES OF CARBON MONOXIDE AND OXYGEN.

By W. E. GARNER AND A. S. GOMM.

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Molecules of carbon dioxide newly formed in the flames of mixtures of carbon monoxide and oxygen emit a fraction of the energy of combination as radiation in the infra-red.<sup>1, 2</sup> The spectrum of this radiation shows marked maxima at  $2\cdot8\mu$  and  $4\cdot5\mu$ . A fraction of this radiation traverses the unburnt gas in front of the flame and is absorbed by carbon monoxide. The absorption bands of carbon monoxide at  $2\cdot3\mu$  and  $4\cdot7\mu$  show very clearly as minima in the emission spectrum of the flame.<sup>1</sup>

The absorption of radiation by molecules of the unburnt gases must facilitate the passage of the flame. This may be a consequence of the increased temperature which occurs on the absorption of radiation, or may be caused by an increased activity of the molecules of carbon monoxide which have absorbed the radiation. The latter effect, as distinct from the purely thermal phenomenon, will be operative only if the activated molecules retain the energy they absorb for a time which is long compared with the average interval between successive collisions. Some experiments by David<sup>3</sup> are suggestive in this connection. Carbon monoxide and air mixtures when insulated previously to ignition with infra-red radiation gave an increased speed of explosion. The increase was out of all proportion to that expected from the rise in temperature which could ensue on insulation.

The study of the effect of the passage of radiation through reacting

<sup>1</sup> Garner and Johnson, *Phil. Mag.*, 1927, **3**, 97.

<sup>2</sup> *J. Chem. Soc.*, 1928, p. 280.

<sup>3</sup> *Proc. Roy. Soc.*, 1925, **A 108**, 617.

mixtures of carbon monoxide and oxygen is on this account of some interest. It is also of importance for the theory of chemical change, for as yet no example of the acceleration of chemical change in homogeneous reactions by the absorption of infra-red radiation has been discovered, in spite of many attempts made during the last few years.

In the following experiments, an attempt has been made to lower the critical pressure of ignition of mixtures of carbon monoxide and oxygen by the passage of infra-red radiation through the reacting gases.

Mixtures of carbon monoxide and oxygen were introduced into a heated

FIG. 1.

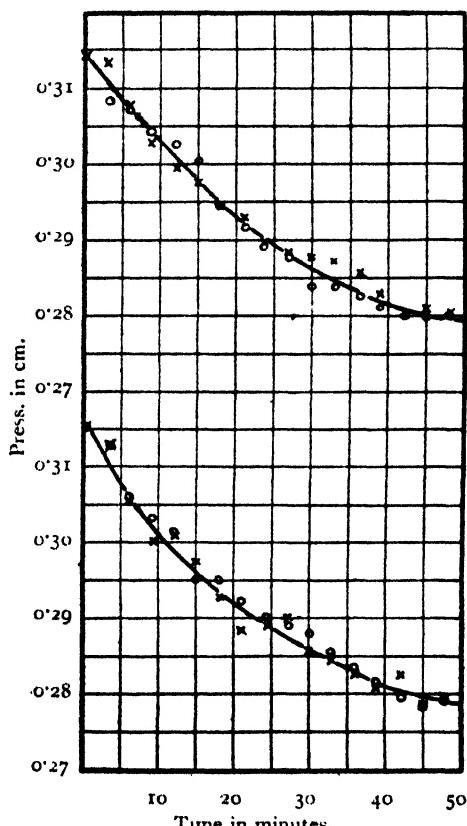
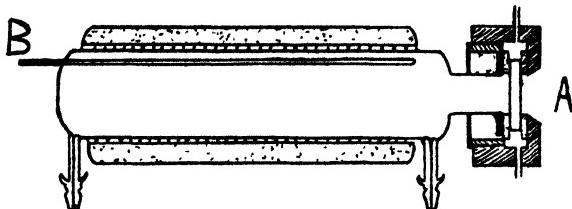


FIG. 2.—Pressure time curves with and without infra-red radiation.

× with infra-red. ○ without red.

ployed, and the gases were dried by passage over ten inches of  $P_2O_5$ . The drying was not intensive. The results of experiments with and without

quartz vessel at a temperature of  $750^\circ$ , the pressure of the gas being maintained just below the critical pressure of ignition, for this temperature. The rate of reaction was measured and compared with that obtained in experiments at the same temperature and pressure when infra-red radiation streamed through the explosive mixture. The temperature in the latter case was adjusted while infra-red radiation was passing through the apparatus, but before the admission of the gas. The quartz apparatus is shown in Fig. 1. The radiation was admitted through the fluorite window A of aperture 1.5 cm., and the temperature measured by a thermocouple placed on tube B, which was in such a position that no radiation fell on the thermocouple. The infra-red radiation was obtained from a furnace at  $1100^\circ C$ , which delivered radiant energy into the apparatus at about 200 cal. per minute. The reaction was followed by pressure measurements. Carbon monoxide and oxygen in equivalent proportions, 2 : 1, were em-

## INITIATION OF FLAME IN MIXTURES

radiation at a temperature of  $750^{\circ}$  and at 0.3 cm. pressure are shown in Fig. 2.

There is no appreciable effect ascribable to the infra-red radiation. The molecules of carbon monoxide absorbing radiation at  $2.3\mu$  and  $4.7\mu$  are not sufficiently activated by the radiation to cause the inception of flame.

Incidentally, data have been obtained on the variation of the critical pressure of ignition with temperature. Both for moderately dry gases and those saturated with water vapour, the critical pressure is practically independent of temperature (Tables I. and II.).\* This is of interest in

TABLE I.—IGNITION PRESSURE OF DRIED  $2\text{CO} + \text{O}_2$ .

Temperature.	Initial Pressure.	Result.
660° C.	3.0 cm. Hg	Ignition
	1.01	"
	0.50	Partial ignition
750° C.	1.03	Ignition
	0.52	Partial ignition
	0.32	No ignition
850° C.	1.05	Ignition
	0.55	"
	0.324	No ignition
	0.223	" "

TABLE II.—IGNITION PRESSURE OF MIXTURE SATURATED WITH WATER VAPOUR.

Temperature.	Initial Pressure.	Result.
660° C.	1.01 cm. Hg	Ignition
	0.50	On point of ignition
750° C.	1.03	Ignition
	0.52	Partial ignition
	0.32	No ignition
850° C.	1.03	Ignition
	0.55	"
	0.324	Partial ignition
	0.223	No ignition

connection with the theory of the combustion process put forward by Semenoff,<sup>4</sup> in which he contrasts the thermal theory of flame propagation with a theory based on a chain mechanism, *i.e.*, on collisions of the second kind, during which the chemical and activation energy held by the products is handed on to one or more reactants. On the latter, but not on the former theory, the critical pressure should be independent of the temperature.

The results given in Tables I. and II. were repeated several times at each temperature. The ignition pressure lies between 0.5 and 0.3 cm. Hg. for the range of temperature 660-850° C., and decreases but slightly over this range. The ignition pressure is the same for the dried as for the moist gases but the rate of the heterogeneous reaction on the surface of quartz is somewhat greater when water vapour is present.

\* Semenoff states that unpublished work by Sagulin shows that this is the case.

<sup>4</sup> Z. Physik, 1928, 48, 571.

The reaction between carbon monoxide and oxygen in quartz vessels has been shown by Bodenstein<sup>5</sup> to be heterogeneous. From our experiments it is heterogeneous at temperatures up to 580° and even above this temperature if the pressure is below 0·3 cm., although there is some evidence from the pressure time curves at 850° that reaction also occurs in the gas phase. When the rate of surface reaction exceeds a certain value, a change is initiated in the gas phase which is rapidly accelerated and is propagated as flame. The surface reaction does not appear to influence the ignition phenomena beyond supplying sufficient energy to set in train the reactions in the homogeneous phase. As long as the minimal energy is available, and the pressure is above the critical pressure, the flame makes its appearance. The supply of larger amounts of energy by the surface reaction does not lower appreciably the pressure at which ignition will occur at any temperature. The limiting pressure of ignition is a property of the homogeneous phase, and therefore the arguments of Semenoff, which concern the reaction in the gaseous phase, should apply to our experiments. The constancy of the ignition pressure may therefore mean that the inception of flame is due to a chain mechanism. One must distinguish, however, between the reactions taking place in gaseous phase prior to ignition and those occurring in the flame itself. It is possible that the mechanism at the higher temperatures of the flame may be different from those at the lower temperatures of the pre-ignition period. The rapidity of thermal interchange is much enhanced the higher the temperature and the transference of energy from burning to unburnt layers of the gas may be of a more thermal character than in the initial period of flame. New experimental evidence in support of this view will be brought forward in a later paper.

It is difficult to reconcile Semenoff's theory of the combustion process with the fact that moist and dried gases give practically the same ignition pressure. If, as is generally agreed, the mechanism of the reactions in the two cases are different, it is not clear why two different chain mechanisms should lead to the same ignition pressures.

The authors are indebted to Imperial Chemical Industries Ltd., for a grant for the purchase of apparatus.

<sup>5</sup> *Z. physik. Chem.*, 1905, 53, 166.

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## THE EFFECT OF HYDROGEN ION CONCENTRATION ON OVERPOTENTIAL.

F. P. BOWDEN.\*

*Received 7th August, 1928.*

There is at the present time considerable difference of opinion as to the relation between hydrogen overpotential and the hydrogen ion concentration of the electrolyte.<sup>1</sup> Glasstone using a lead cathode in sulphuric acid

\* Communicated by Dr. E. K. Rideal.

<sup>1</sup> *J. Chem. Soc.*, 125, 2646, 1924.

of concentration varying from  $N/1$  to  $N/16$  found the overpotential<sup>2</sup> to be independent of the concentration of the acid. The current density employed was greater than  $10^{-4}$  amps. cm.<sup>2</sup> and the overpotential was 0·6 to 0·8 volts. He arrives at similar conclusions for a mercury cathode, but from the figures given there is a considerable increase in the overpotential as the acidity decreases, for current densities of the order of  $10^{-3}$  amps. cm.<sup>2</sup>. At lower current densities, however, the figures given by Glasstone agree well and show no change of overpotential over a range of hydron concentration from  $N/1$  sulphuric acid to  $N/1$  NaOH. The actual current density employed is not stated, but the potential selected in the case of each electrolyte is that at which bubble evolution is first observed on the mercury surface and this is defined as the "minimum overvoltage." The selection of this point is rather arbitrary and, as Glasstone states,<sup>1</sup> it is difficult to determine it with any accuracy. The conclusion arrived at is that hydrogen overpotential is independent of the hydrogen ion concentration of the solution.

On the other hand, Hérovsky, using a dropping mercury electrode, finds a considerable increase in the hydrogen overpotential with decreasing acidity and postulates a shift in the overpotential equal to that observed in the reversible hydrogen electrode.<sup>3</sup> This has been experimentally investigated by Heyrasymenko<sup>4</sup> for solutions in which the hydrogen ion concentration varied from  $p_H\ 1$  to  $p_H\ 7$ . The polarising current  $i$  was plotted against the potential  $\pi$  of the cathode, for each solution and points on the respective curves were selected at which  $\frac{di}{d\pi}$  had an arbitrary fixed value. The potential at this point was called the "deposition potential of hydrogen" and the increase of this potential of 58 millivolts for every ten-fold decrease of the hydron concentration was verified with considerable accuracy. The current passed was approximately  $10^{-7}$  amps., but the area of the mercury drop is not given so that the current density is not known with certainty. These overpotentials are considerably higher than those measured by Glasstone.

Sand and Weeks<sup>5</sup> in investigating the polarisation of an antimony cathode in alkaline solutions find a *decrease* in the hydrogen overpotential, with decreasing hydrogen ion concentration, but as pointed out by Heyrasymenko<sup>6</sup> the primary process here is in all probability the deposition of sodium. This explanation is not accepted by Sand.<sup>7</sup>

In the course of a general study of the electro-deposition at metallic cathodes it is found that if dissolved oxygen and impurities are rigorously excluded from the cell the deposition of hydrogen can be followed down to very low current densities ( $10^{-8}$  amps. cm.<sup>2</sup>) and when the overpotential is plotted against the logarithm of the current density the points lie accurately on a straight line. The slope of this line is approximately the same for all metals and in acid solutions the relation holds up to high current densities ( $> 10^{-2}$  amps. cm.<sup>2</sup>) when hydrogen is being evolved freely from the cathode.<sup>8</sup> Since the overpotential is a continuous function of the rate of hydrogen deposition it is apparent that no special significance can be attached to the "minimum overvoltage" as defined by Glasstone nor to the

<sup>2</sup> By overpotential is meant here the difference in potential between the cathode and a reversible hydrogen electrode in the same electrolyte.

<sup>3</sup> Rec. Trav. Chim., 44, 499 (1925).

<sup>4</sup> Ibid., 503, (1925).

<sup>5</sup> J. Chem. Soc., 125, 161 (1924).

<sup>6</sup> Rec. Trav. Chim., 44, 503 (1925); 46, 586 (1927).

<sup>7</sup> Ibid., 47, 342 (1927).

<sup>8</sup> Bowden and Rideal, Proc. Roy. Soc., Aug., 1928.

"hydrogen deposition potential" defined by Heyrasymenko. In the case of the latter, since the curve is really logarithmic, the potential selected, depends on the scale on which the curve is drawn and on the arbitrary value chosen for  $\frac{di}{d\pi}$ . This, however, does not necessarily affect the validity

of the conclusion arrived at by these investigators as to the effect of hydrogen ion concentration, since the overpotential selected in each solution is that corresponding to a definite, though arbitrary, rate of hydrogen deposition.

In view of the conflicting evidence on this point and its bearing on the general mechanism of hydrogen deposition, it was necessary to investigate this experimentally. The relation between the overpotential and the current at a mercury cathode was studied in solutions of varying hydrogen ion concentration and over a range of current density of  $10^{-8}$  to  $10^{-3}$  amps. cm.<sup>2</sup>. The potential plotted against the logarithm of the current gave a straight line and conclusions as to the effect of hydrogen ion concentration are based on the shift of the whole line and do not rest on the measurement of single points.

One of the most serious difficulties in the study of electrode phenomena lies in the difficulty of obtaining reproducible results, the presence of traces of impurities<sup>9</sup> or of dissolved oxygen<sup>8</sup> having a very marked effect on the electrode potential. If precautions are taken to eliminate these, reproducible results can be obtained and in the following experiments the reproducibility of each curve was checked by repeatedly filling the cell with one solution and then the other.

#### Apparatus.

In Fig. 1 is shown the cell and the arrangement for filling it without allowing air or mercury ions to enter the electrolyte. Two solutions of

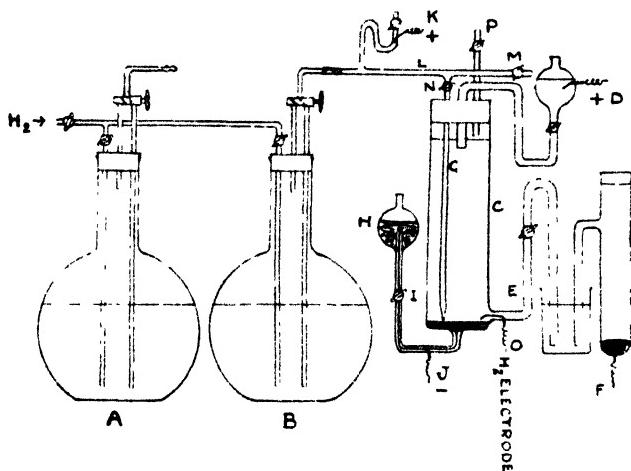


FIG. 1.

different hydrogen ion concentration contained in the flasks A and B are boiled out under reduced pressure and cooled in a hydrogen atmosphere. These flasks are of thick glass since the liquid bumps violently when freed

<sup>9</sup> Bowden, *Trans. Farad. Soc.*, **23**, 571, 1927.

from dissolved gas. The cell C consists of a glass cylinder 10 cm. long by 2·3 cm. diameter with the mercury cathode at the bottom; to prevent contamination by oxygen the platinum anode is sealed into the bulb D and contact is made through a glass tube filled with electrolyte and entering through the centre of the stopper. A side arm E leads out from just above the cathode surface and can be connected to a saturated calomel electrode F. In the bend of this side arm and in the vicinity of the cathode is sealed a platinum wire O coated with platinum black which acts as a hydrogen electrode. The electrolyte is admitted through the tube G which is drawn out to a capillary just above the cathode surface. Mercury in the bulb H can be admitted to the cell by turning the tap I; and contact is made with this mercury by a sealed-in platinum wire J. Both the flasks A and B are fitted with two-way taps by means of which either hydrogen or electrolyte can be forced into the cell.

The procedure is to clean and dry the cell, evacuate and fill with hydrogen which is passed for some time to displace air from the side tubes. The bulb H is then filled with mercury and by turning the tap I some of this is run into the cell. This bulb is so constructed that the mercury which enters the cell comes from the interior of the mass of mercury and so is free from oxide or adsorbed oxygen. Electrolyte is then admitted by turning a two-way tap on one of the flasks. To prevent any mercury ions from entering the solution, the mercury is made cathodic during the filling of the cell; this is done by means of an auxiliary platinum anode sealed into the tube K which enables a polarising current to flow as soon as the electrolyte comes into contact with the mercury. When the cell is filled and connection is made with the main anode in D, this auxiliary anode is disconnected. P is an outlet for hydrogen. After measurements have been made on one electrolyte this is forced out through the side arm E by hydrogen and the other electrolyte run in. The cell is repeatedly emptied and refilled with the fresh electrolyte in order to wash it out and finally refilled. In changing over from one flask to the other a little air may enter the tube L, so a stream of hydrogen is blown through this and out the bye-pass tap M before the tap N is opened. When the cell is filled all the taps are kept closed since sufficient current can be passed with them in this position. The potential of the mercury cathode is measured against the reversible hydrogen electrode O. The hydrogen ion concentration of the electrolyte is determined by measuring the potential of this hydrogen electrode against the saturated calomel electrode F.

The general arrangement of the apparatus is similar to that previously described,<sup>8</sup> an Einthoven string galvanometer and a potentiometer being used for the measurement of the potentials. The polarising current is supplied by a 50-volt battery of small accumulators, the smaller current being measured by a uni-pivot galvanometer (1 div. =  $5 \times 10^{-8}$  amps.).

The mercury was purified by distillation followed by prolonged agitation with air and mercurous nitrate and finally by redistillation under reduced pressure with a slow current of air bubbling through it. The water was purified by redistillation in a silica still, the sulphuric acid by distillation in pyrex glass and the chemicals used in making the buffer solutions by double recrystallisation. The hydrogen from a cylinder was passed through wash bottles to remove carbon dioxide and a long train of heated palladinised copper to remove oxygen. The stoppers for the flasks and the cell were of rubber but they were cleaned with alkali and with acid and the electrolyte was not allowed to come into contact with them. The cell was of soda glass and all the glass ware was cleaned with chromic acid and distilled water be-

fore use. The experiments were carried out in a basement where the air temperature was fairly constant *ca.* 18° C.

### Experimental.

Measurements of the hydrogen overpotential over a current density range of  $10^{-3}$  to  $10^{-2}$  amps. cm.<sup>2</sup> have been made with electrolytes of dilute sulphuric acid, of dilute sulphuric acid in  $N/10$  KCl and of buffer solutions in  $N/10$  KCl.

Three solutions were made up from citric acid and sodium phosphate<sup>10</sup> in  $N/10$  KCl.

	Approximate Composition.	Potential of Hydrogen Electrode against Saturated Calomel.	$\rho_{H^+}$
Solution <i>a</i>	0.2 M Na <sub>2</sub> HPO <sub>4</sub> 0.4 parts 0.1 M citric acid 19.6 parts + N/10 KCl	0.376	2.2
Solution <i>b</i>	0.2 M Na <sub>2</sub> HPO <sub>4</sub> 7.7 parts 0.1 M citric acid 12.3 parts + N/10 KCl	0.494	4.2
Solution <i>c</i>	0.2 M Na <sub>2</sub> HPO <sub>4</sub> 16.4 parts 0.1 M citric acid 3.6 parts + N/10 KCl	0.631	6.6

In figures 2, 3 and 4 respectively the logarithm of the current density in amps.  $\times 10^{-7}$  is plotted against the over-potential for these three solu-

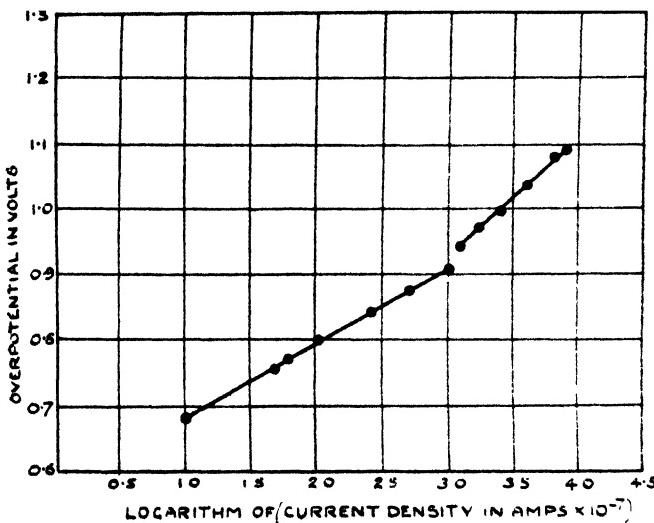


FIG. 2.

tions. For each solution the curves have been checked several times by running in first one and then the other to ensure that no change has occurred in

the mercury surface and also by completely emptying the cell and running in a fresh cathode. The agreement under duplicate conditions was to  $\pm 10$  m. v.

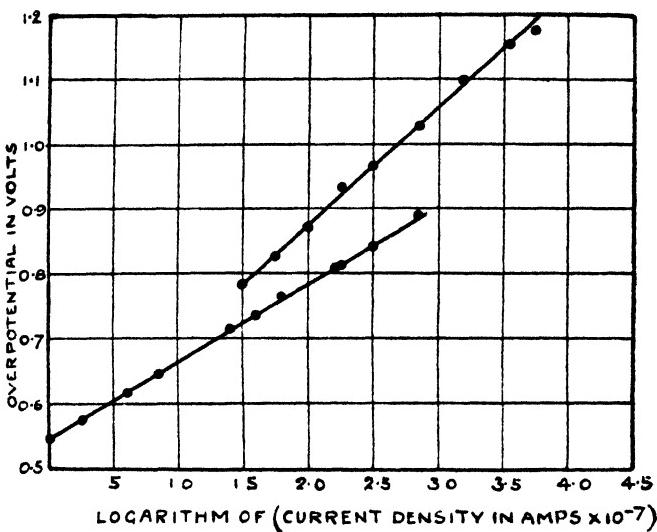


FIG. 3.

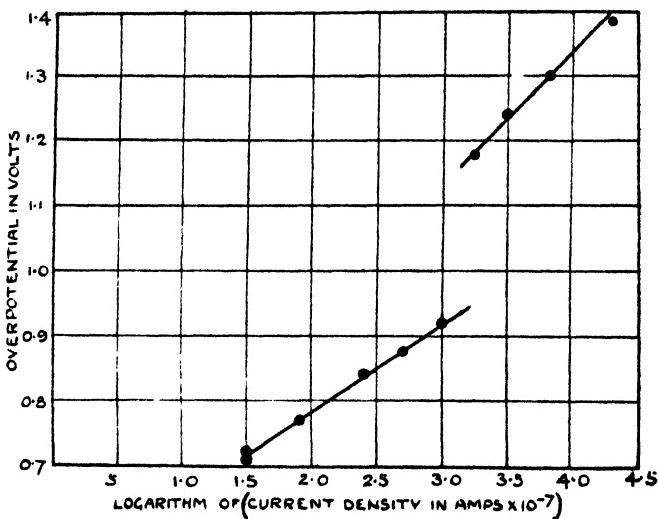


FIG. 4.

In each case the points lie on straight lines and the graphs fall into two distinct parts. In part (i) the slope of the line or  $\frac{d\eta}{d \log i}$  equals 0.120; in part (ii) the slope equals ca. 0.220. The point at which the break occurs

is not very definite but it generally takes place at an overpotential of about 0.9 volts.<sup>11</sup>

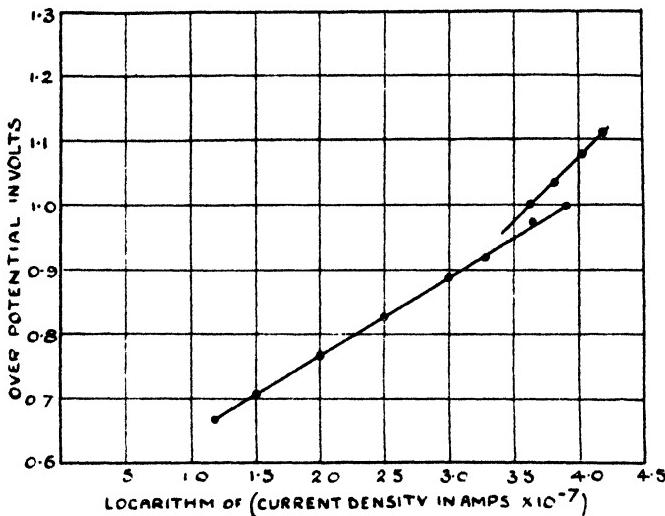


FIG. 5.

Measurements were also made with an electrolyte of dilute sulphuric acid of  $\rho_H$  0.8, solution *d*, Fig. 5 : of dilute sulphuric acid in *N*/10 KCl of

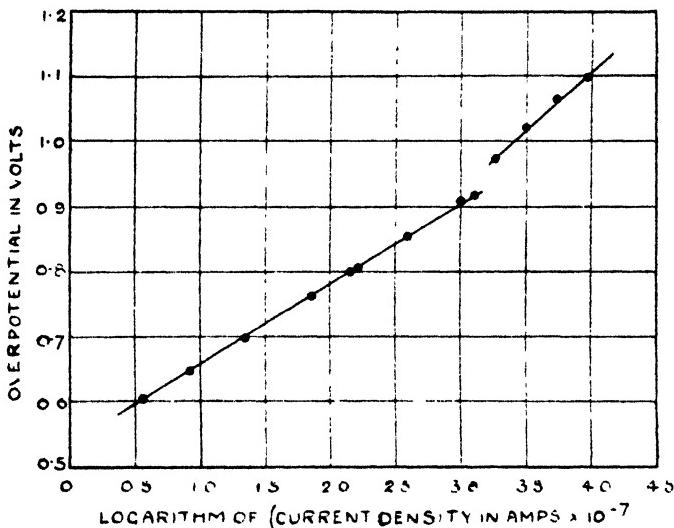


FIG. 6.

$\rho_H$  2.5, solution *e*, Fig. 6 : and of a buffer solution of normal and acid sodium phosphate in *N*/10 KCl of  $\rho_H$  4.4, solution *f*, Fig. 7.

<sup>11</sup> In some unpublished work McAulay and Mellor have observed a similar break at about this potential.

All these curves have the same characteristics, showing that the effect observed is not due to a particular composition of electrolyte nor to impurities.

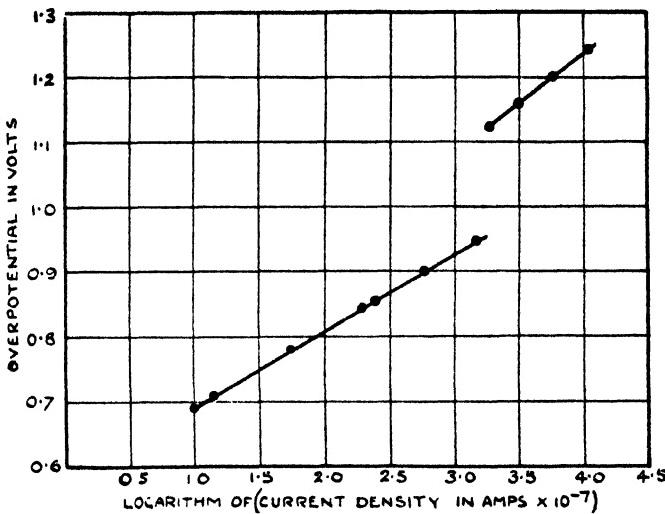


FIG. 7.

In Fig. 8 the curves for all these solutions are plotted on the same figure.

It is seen that part (i) of the curves are approximately coincident for all the solutions, showing that although the potential of the hydrogen electrode

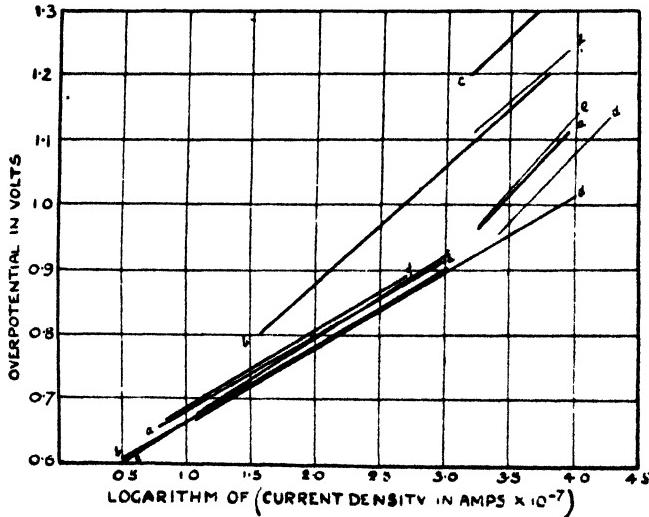


FIG. 8.

varies by as much as 300 milli-volts the overpotential over this range is independent of the hydrogen ion concentration of the solution. On part (ii) of the curves, however, the overpotential increases with decreasing

hydrogen ion concentration and it is seen from the following table that the shift is approximately the same as that occurring in the reversible hydrogen electrode, being about 58 milli-volts per ten-fold decrease in the hydrogen ion concentration.

	Potential of Reversible Hydrogen Electrode against Saturated Calomel.	Change in Hydrogen Electrode Potential.	Change in Over-potential.
Solution (a)	0·376	—	—
" (b)	0·494	0·118	0·130
" (c)	0·631	0·255	0·240
" (d)	0·300	- 0·075	- 0·050
" (e)	0·392	0·017	0·010
" (f)	0·503	0·128	0·140

That the primary process occurring on part (ii) of the curve is also the deposition of hydrogen is shown by the fact that the shift of the curve follows only the hydrogen ion concentration, being otherwise independent of the composition of the electrolyte. Also Heyrasymenko<sup>4</sup> has shown that the deposition of the sodium ion from  $N/10$  NaCl does not occur until a potential of 1·9 volts sat. cal. is reached whereas the break can occur at a potential of less than 1·3 volts sat. cal. which is 600 milli-volts below this.

It is found that with dilute unbuffered solutions the observed shift in overpotential on part (ii) of the curve is somewhat greater than that calculated, but in this case it is very probable that the hydrogen ion concentration in the immediate vicinity of the cathode is less than that in the bulk of the solution, owing to concentration polarisation. The point at which the break in the curve occurs is rather indefinite but with acids stronger than  $N/10$  it only occurs at very high current densities. It is interesting that once the break has occurred the current density can frequently be reduced to a low value without the curve reverting to the slope characteristic of part (i). This is shown clearly in Fig. 3 : as the polarising current was increased from a low value no break occurred until the current density reached a value of  $10^{-4}$  amps. cm.<sup>2</sup>, with an overpotential of 0·9 volts. On now decreasing the current the potential followed the curve with a slope and value characteristic of part (ii) down to a very low value of the current density. This behaviour is frequently observed and over this range the potential can drop suddenly from that characteristic of part (ii) to that of part (i). In general the slope of the curve is either that characteristic of part (i) or of part (ii), but curves having a slope intermediate between these two values have been obtained.

The reason for the divergence of opinion between different investigators is now apparent. The value of the "minimum overvoltage" selected by Glasstone was 0·76 volts, which from Fig. 8 would lie on part (i) of the curve and correspond to a current density of ca.  $5 \times 10^{-6}$  amps. cm.<sup>2</sup>; this would show no shift with changing hydrogen ion concentration. The values for the "deposition potential" selected by Heyrasymenko were greater than this and lay on part (ii) of the curve. For example, with a buffer solution of hydron concentration  $1·6 \times 10^{-4}$  the overpotential was 0·93, which from Fig. 8 would lie on part (ii) of the curve and correspond to a current density at a stationary cathode of  $2 \times 10^{-5}$  amps. cm.<sup>2</sup>.

### Experiments with Dropping Cathode.

In order to confirm these conclusions the behaviour of a dropping cathode was studied over a considerable range of current density. It was expected that if the logarithm of the current were plotted against the potential a straight line would result having a slope of  $\approx 0.220$  corresponding to part (ii) of the curves and showing a shift of overpotential with changing hydrogen ion concentration.

A modification of Hérovsky's dropping cathode was set up and this is shown in Fig. 9.

The cell consisted of a glass cylinder A drawn off to a long narrow glass tube B which was closed at the bottom by a tap. The purified mercury was contained in the glass bulb C which was connected to the drawn out capillary tube D. The rate at which mercury dropped from

this capillary was controlled by varying the air pressure in C. This pressure was altered by raising or lowering a second bulb of mercury E which was connected to L by a flexible rubber tube. In this way contact of the cathode mercury with rubber tubing and possible contamination by impurities was avoided. Electrical connection to the mercury cathode was made by the platinum wire sealed in at F.

The anode of the cell was a platinum wire G sealed into the right hand arm of the tube H. The left hand arm of this tube led to the flasks containing the oxygen free electrolyte and by means of two-way taps either hydrogen or electrolyte could be forced into the cell. With this arrangement the mercury could be made cathodic during the actual filling of the cell and the electrolyte was kept free

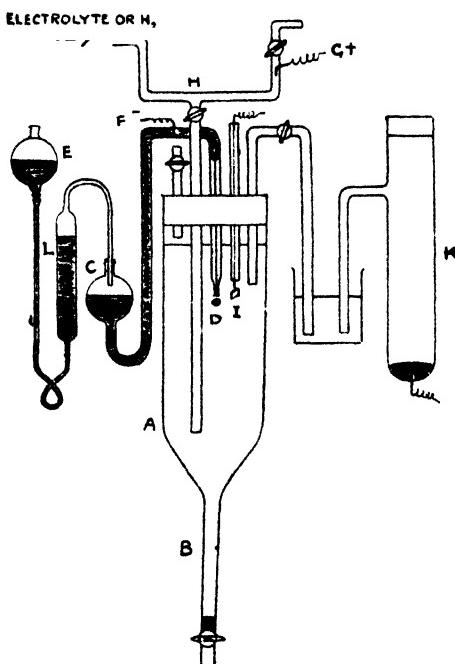


FIG. 9.

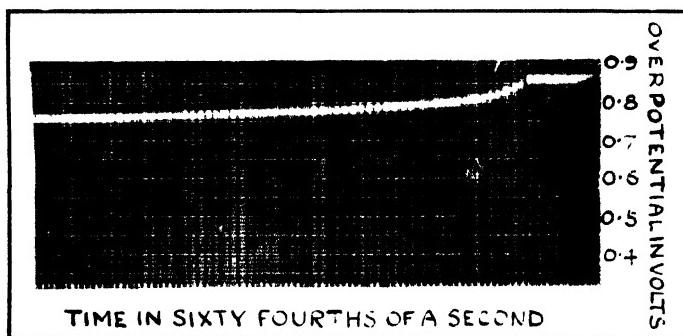
from mercury ions or oxygen. The mercury drops fell to the bottom of the long tube B so that any mercury ions which went into solution from this could not diffuse to the vicinity of the cathode during the time of the experiments. The potential of the cathode was measured against the hydrogen electrode I or against the calomel electrode K, connection in the latter case being made by a glass tube L, leading from the vicinity of the cathode. The hydrogen electrode I consisted simply of a strip of platinised platinum; it was found unnecessary to bubble hydrogen past it. In a solution which has been carefully freed from oxygen and saturated with hydrogen the potential of a strip of platinised platinum will remain constant for days at that characteristic of the hydrogen electrode without any additional hydrogen being supplied.

The measurements were made in buffer solutions similar to those used with the stationary cathode.

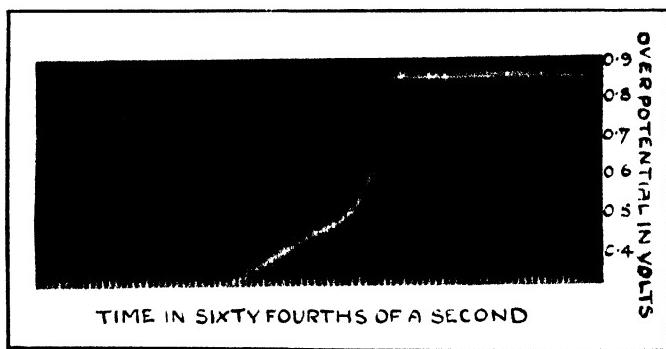




FIG. 10.



Curve 1.



Curve 2

FIG. 12.

[To face page 483.]

	Approximate Composition.	Potential of Reversible Hydrogen Electrode.	$p_{H^+}$
Solution <i>g</i>	0.2 M Na <sub>2</sub> HPO <sub>4</sub> 0.4 parts 0.1 M citric acid 19.6 parts + N/10 HCl	0.370	2.1
Solution <i>h</i>	0.2 M Na <sub>2</sub> HPO <sub>4</sub> 4.0 parts 0.1 M citric acid 16.0 parts + N/10 HCl	0.414	2.8

### Experimental.

With solution *h* on passing a current of  $4 \times 10^{-6}$  amps. the overpotential rose to *ca.* 0.99 V and fluctuations of 150 milli-volts occurred as the drop grew in size and broke away. This is shown in Fig. 10, the drop rate being *ca.* 4 drops in 3 seconds.

At the point A the drop broke away from the capillary and the overpotential rose rapidly to a maximum from which it slowly decreased as the drop increased in size. The diameter of the orifice in the capillary tube from which the mercury issued was *ca.*  $5 \times 10^{-3}$  cm., but an examination

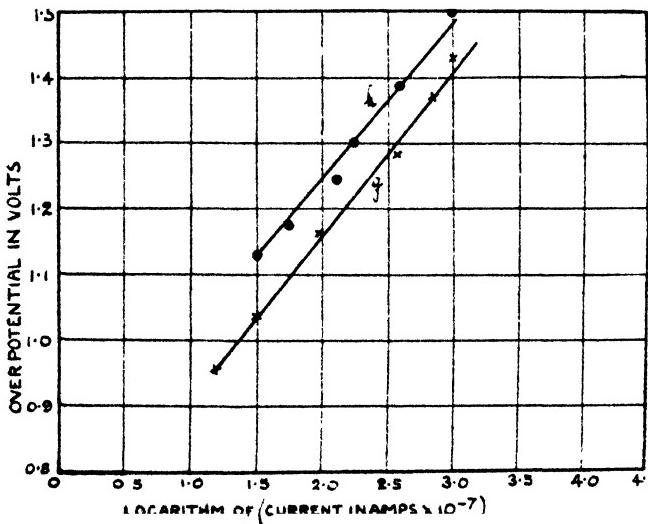


FIG. XI.

of the falling drop under a low power microscope showed that the drop did not break clean away from the capillary but left a small drop of area *ca.*  $3 \times 10^{-4}$  cm.<sup>2</sup> adhering to the tube. The radius of this drop increased until it was *ca.*  $4 \times 10^{-2}$  cm. (area  $2 \times 10^{-2}$  cm.<sup>2</sup>) when it broke away and the process was repeated. The change in current density due to this change in drop size is from  $1.3 \times 10^{-8}$  amps. cm.<sup>2</sup> to  $2 \times 10^{-4}$  amps. cm.<sup>2</sup>. It will be seen from Fig. 10 that this change in current density can cause a change of 170 milli-volts so that the observed fluctuations in the potential are due to this effect. In plotting the logarithm of the current against the

potential the value of the latter is taken when the drop is at its maximum size, *i.e.*, at the point A on Fig. 10.

The behaviour in solution g is similar and in Fig. 11 the logarithm of the current density is plotted against the overpotential for these two solutions.

It is seen that for currents greater than  $10^{-6}$  amps. and over a range which includes the potential measured by Heyrasymenko, the points lie approximately on a straight line having a slope of *ca.* 0.220 and show a shift in the overpotential of *ca.* 58 milli-volts per ten-fold dilution, thus confirming the previous conclusions.

With currents smaller than  $10^{-6}$  amps. the points fall below the straight line and at lower current densities the potential is variable. Apparently at this low current density the growing drop breaks away before the potential has time to reach its equilibrium value. It is probable that if the equilibrium potential were measured over this range it would lie on part (i) of the curve and show no shift of overpotential with changing hydron concentration.

### Conclusion.

In general the relation between hydrogen overpotential  $\eta$  and the current density  $i$  is given by

$$\eta = a_1 + b \log i \quad . . . . . \quad (i)$$

where  $a_1$  and  $b$  are constants, and in acid solutions this relation holds over a very wide range of current density. If, however, a certain rate of hydrogen deposition is exceeded or if the hydrogen ion concentration of the solution is reduced, the relation becomes

$$\eta = a_2 + 2b \log i \quad . . . . . \quad (ii)$$

On increasing the current density in a solution of definite hydrogen ion concentration a point is reached at which the relation changes from (i) to (ii) and the lower the hydrogen ion concentration the lower the current density at which this occurs. Over (i) the hydrogen overpotential for a given current density is independent of the hydrogen ion concentration of the solution. Over (ii) the overpotential increases with decreasing hydrogen ion concentration, showing approximately the same shift as the reversible hydrogen electrode. It is possible that over part (i) the potential supply of hydrogen ions to the cathode exceeds the rate at which the reaction is occurring on the cathode surface so that over this range variations in the hydrogen ion concentration will have no effect. When, however, the reaction velocity exceeds a certain value or if the hydrogen ion concentration is reduced so that they are no longer present in excess at the cathode surface the overpotential is influenced by the hydrogen ion concentration. At the same time  $b$  changes to twice its initial value. The bearing of this on the mechanism of hydrogen deposition will be considered in more detail later, but it may be noted that the value of  $b$  is numerically equal to  $\frac{2RT}{F}$ , *viz.*, 0.116.

### Transfer Resistance.

The main evidence for the existence of a transfer resistance at the surface of metallic cathodes during the deposition of hydrogen is found in the work of Newbery. He finds that on opening the polarising circuit there is

a large instantaneous drop in the overpotential followed by a more gradual decay. The initial rapid drop is attributed to transfer resistance. The magnitude of this transfer resistance increases with decreasing current density and the value calculated at a mercury cathode for a current of  $10^{-3}$  amps. cm.<sup>2</sup> is 100 ohms per sq. cm.<sup>12</sup> This would correspond to an instantaneous potential drop of 100 milli-volts; at higher current densities the potential drop varies from 0.5 to 2 volts.

In the course of this present investigation and in previous work, the behaviour of metallic cathodes on open circuit has been studied. The shadow of the fibre (period 1/300 sec.) of the Einthoven galvanometer is thrown on a moving film camera and the fall of potential measured. The sensitivity of the galvanometer is high so that less than  $10^{-7}$  amps. are drawn from the test cathode. If dissolved oxygen and metal ions are rigorously excluded from the electrolyte the decay of overpotential is comparatively slow and can be followed from the moment of opening the circuit; there is no instantaneous drop as would be expected if part of the cathode potential were due to transfer resistance. This is true whether the potential is measured on part (i) or part (ii) of the curve. In general the higher the overpotential the more rapid is the initial decay, but it can be followed easily for overpotentials of one volt at a mercury cathode in  $N/10$  sulphuric acid when hydrogen bubbles are being freely evolved. In solutions of lower acidity the decay is even slower; in fact approximate calculations show that the observed drop in potential is that which would be expected from an estimation of the amount of hydrogen removed from the surface due to natural decay, this being calculated from a measurement of the rate of hydrogen evolution at each potential and the relation between the potential and the surface concentration of hydrogen.<sup>8</sup>

If, however, very small amounts of dissolved oxygen or of metal ions are present in the electrolyte the initial rate of fall of the overpotential is too rapid to be recorded and the photographs resemble those obtained by Newbery.

This is shown in Fig. 12.

Curve I shows the natural decay from an overpotential of 0.88 V. in a citric buffer solution of  $\rho_H$  4.2 which has been freed from oxygen. The current density is  $4 \times 10^{-5}$  amps. cm.<sup>2</sup> and at the point A the circuit is opened. The marks at the bottom of the photograph represent the time in sixtieths of a second. Curve II. shows the decay from the same overpotential in the same solution except that it is not freed from oxygen and the anode is placed in the same compartment as the cathode.

In a more recent paper Newbery has found that included in the potential drop previously attributed to transfer resistance was a considerable potential due to the resistance of the electrolyte. The geometry of the cell was such that the tube leading to the standard electrode was some distance from the cathode so that the potential measured included an ohmic drop through the electrolyte due to the passage of the polarising current. With a modified form of cell the values found for the transfer resistance are in general considerably lower, but even with this the value at a silver cathode with a current density of  $10^{-3}$  amps. cm.<sup>2</sup> is calculated as 40 ohms per sq. cm. This transfer resistance is attributed to the formation of a non-conducting film of gas over the cathode surface which impedes the passage of the current, and variations which occur in the overpotential are attributed to changes occur-

<sup>12</sup> Newbery, *Proc. Roy. Soc., 107A*, 486, 1926.

ring in the thickness and hence the resistance of this gas film. In some quantitative measurements made on the relation between the overpotential and the amount of hydrogen deposited it is found<sup>8</sup> that in establishing the overpotential the deposition of sufficient hydrogen equivalent to only  $1/3000$ th of an atomic layer causes an increase of 100 milli-volts in the potential. It is apparent that this quantity of gas is not sufficient to cause any appreciable alteration in the thickness of a complete protective film such as that postulated to explain transfer resistance. It is possible that with prolonged electrolysis and high current densities hydrogen bubbles can collect on the cathode surface and partially protect it, so giving rise to a transfer resistance; this however would be a secondary effect, having only an indirect bearing on the mechanism of the electrodeposition of hydrogen.

### Summary.

The relation between the hydrogen overpotential at a mercury cathode and the hydrogen ion concentration of the electrolyte is studied in solutions which are free from dissolved oxygen or metal ions. The relation between the overpotential  $\eta$  and the current density  $i$  is given by  $\eta = a_1 + b \log i$ , where  $a_1$  and  $b$  are constants, and in acid solutions this holds for current densities of  $10^{-8}$  amps. cm.<sup>2</sup> where the overpotential is small to  $> 10^{-2}$  amps. cm.<sup>2</sup> where the overpotential exceeds one volt and hydrogen is being freely evolved. No special significance can be attached to the terms "minimum overvoltage" or "hydrogen deposition potential." Over this range the overpotential is independent of the hydrogen ion concentration. If a certain rate of deposition is exceeded or if the hydrogen ion concentration is reduced below a certain value the relation becomes  $\eta = a_2 + 2b \log i$  and over this range the overpotential increases with the decreasing hydrogen ion concentration showing the same shift as a reversible hydrogen electrode. No evidence is found for transfer resistance.

My best thanks are due to Dr. E. K. Rideal for continued interest and encouragement in these problems and to the Commissioners of the 1851 Exhibition for a Scholarship under which this work was carried out.

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## THE DECOMPOSITION OF HYDROGEN PEROXIDE IN PRESENCE AND IN THE ABSENCE OF SODIUM HYDROXIDE.

By CONSTANTIN PANA.\*

*Received 1st August, 1928.*

The decomposition of hydrogen peroxide in aqueous solution has been studied by numerous workers. Several contributions to the study of the decomposition of hydrogen peroxide in alkaline solution have likewise been made, and certain conclusions drawn. Thus, Schöne<sup>1</sup> emphasised the formation of alkaline peroxides which act as intermediate complexes in the

\* Communicated by Professor W. C. M. Lewis.

<sup>1</sup> Schöne, *Annalen*, 192, 257 (1878); *ibid.*, 193, 241 (1878).

decomposition. Tammann<sup>2</sup> concluded that bases accelerate the decomposition of hydrogen peroxide, the decomposition being independent of the nature and amount of alkali. Lemoine<sup>3</sup> has shown that bases increase considerably the decomposition owing to the formation of sodium peroxide. Also he concluded that the water itself catalyses the decomposition. Clayton<sup>4</sup> concludes that the effect of alkali is partly due to the ferric hydroxide present as impurity. Finally, Burki and Schaaf<sup>5</sup> as a result of their experiments conclude that the velocity of decomposition of the  $H_2O_2$  is proportional to the concentration of base but is independent of the nature of the cation present. They consider the surface action of the glass reaction vessel to be negligible, but found that temperature has considerable influence on the reaction.

The work described below has been carried out with the view of ascertaining the variation in the rate of decomposition in alkaline solution in relation to the concentration of hydrogen peroxide and the concentration of sodium hydroxide; also the influence of temperature, the surface of the reaction vessel, and the effect of the dust normally present in aqueous and other liquid systems.

### Experimental.

A concentrated solution of *sodium hydroxide* was prepared directly from metallic sodium and this was diluted with conductivity water to the strength required for the experiments, viz.: 0.008 N, 0.013 N, 0.025 N. The solution contained minute traces of iron.

The *hydrogen peroxide*, prepared from sulphuric acid and sodium peroxide, was redistilled under 26 mm. pressure at 68° C. The concentrations of hydrogen peroxide employed were 0.5 N and 1.5 N.

Samples of hydrogen peroxide were tested from time to time for chlorides and sulphates, but in no case were they found.

Freshly-distilled conductivity *water* was used (specific conductivity at 25° C. =  $8 \times 10^{-7}$ ).

The melting-point of the wax employed (to coat the interior of the vessels in certain experiments) was found to be 60° C. The wax was found to be slightly acid and of a high degree of saturation.

The effect of surfaces of different kinds has been observed by employing containing vessels of (*a*) glass, (*b*) glass coated with wax, (*c*) silica.

The reaction-flasks were freshly blown from glass boiling tubes. They were cleaned before use with cold chromic acid, washed thoroughly with distilled water, finally being steamed and dried in an air-oven. Each reaction-flask was fitted with an air condenser to prevent any evaporation of the liquid solvent, and also with a siphon tube to facilitate the withdrawal of the liquid. 2 c.c. of the solution were withdrawn and titrated against a solution of  $KMnO_4$ . The results are tabulated below. The values are the means of several concordant sets of measurements.

<sup>2</sup> Tammann, *Z. physikal. Chem.*, 4, 441 (1889).

<sup>3</sup> Lemoine, *J. Chimie Phys.*, 12, 1 (1914); *Compt. Rend.*, 161, 47 (1915).

<sup>4</sup> Clayton, *Trans. Faraday Soc.*, 11, 164 (1915).

<sup>5</sup> Burki and Schaaf, *Helv. Chim. Acta*, 4, 418 (1921).

## DECOMPOSITION OF HYDROGEN PEROXIDE

The Decomposition of  $H_2O_2$  in Absence of Alkali.

TABLE I.—CONCENTRATION OF HYDROGEN PEROXIDE = 0·5 NORMAL.

Nature of Surface.	Initial Rate of Decomposition, g. $H_2O_2$ /c.c./minute $\times 10^{-6}$ .		
	40° C.	50° C.	60° C.
Silica . . .	0·63	1·40	2·27
Glass . . .	0·274	0·64	1·35
Wax . . .	0·075	0·18	—

The observed decomposition in wax-lined vessels is ascribed to the dust present in the solution. By subtraction, the true effects due to glass and silica respectively can thus be calculated. In this way, the results given in Table II. are obtained.

TABLE II.—CONCENTRATION OF HYDROGEN PEROXIDE = 0·5 NORMAL.

Effect Due to:	Initial Rate of Decomposition, g. $H_2O_2$ /c.c./minute $\times 10^{-6}$ .			E 40°/50° Calcs.
	40° C.	50° C.	60° C.	
Silica alone .	0·555	1·22	—	15,700
Glass , ,	0·199	0·46	—	16,800
Dust , ,	0·075	0·18	—	17,500

TABLE III.—CONCENTRATION OF HYDROGEN PEROXIDE = 1·5 NORMAL.

Nature of Surface.	Initial Rate of Decomposition, g. $H_2O_2$ /c.c./minute $\times 10^{-6}$ .		
	40° C.	50° C.	60° C.
Silica . . .	0·38	0·89	1·90
Glass . . .	0·135	0·325	0·70
Wax . . .	0·03	0·08	—

TABLE IV.—CONCENTRATION OF HYDROGEN PEROXIDE = 1·5 NORMAL.

Effect Due to:	Initial Rate of Decomposition, g. $H_2O_2$ /c.c./minute $\times 10^{-6}$ .			E 40°/50° Calcs.
	40° C.	50° C.	60° C.	
Silica alone .	0·35	0·81	—	16,800
Glass , ,	0·105	0·245	—	17,000
Dust , ,	0·03	0·08	—	18,000

Examination of Table IV. reveals that a silica vessel exerts a greater catalytic effect on the decomposition than a glass vessel. The latter in turn exerts a greater effect than dust, i.e., a wax-lined vessel. Attention might

be drawn at this point to certain results obtained by B. H. Williams<sup>6</sup> who, working with materials prepared in a manner similar to that of the writer and under analogous conditions, but at 50° C., obtained results in silica, glass and wax vessels. From the initial rates and critical increments recorded by Williams, it is possible to compare his calculated rates of reaction at 50° with those of the writer. The initial rates of reaction in both cases are of the same order of magnitude, but the initial rates of decomposition calculated from Williams' data, are in all cases higher than those recorded by the author. The relative surface catalytic effects as found by Williams are silica > dust > glass. Possibly this difference from the finding of the writer (namely silica > glass > dust) may be due to differences in the dust content of the solutions employed by Williams and the writer.

### The Decomposition of $H_2O_2$ in Presence of Alkali.

TABLE V.—CONCENTRATION OF HYDROGEN PEROXIDE = 0·5 NORMAL.

Nature of Surface.	(NaOH) Normality.	Initial Rate of Decomposition, g. $H_2O_2$ /c.c./minute $\times 10^4$ .		
		40° C.	50° C.	60° C.
Silica . . .	0·008	1·56	3·23	6·175
	0·013	3·35	6·20	10·45
	0·025	5·30	9·72	16·25
Glass . . .	0·008	0·585	1·35	2·73
	0·013	1·40	2·875	5·30
	0·025	2·25	4·40	7·575
Wax . . .	0·008	0·16	0·37	—
	0·013	0·33	0·70	—
	0·025	0·58	1·17	—

TABLE VI.—CONCENTRATION OF HYDROGEN PEROXIDE = 0·5 NORMAL.

Effect Due to:	(NaOH) Normality.	Initial Rate of Decomposition, g. $H_2O_2$ /c.c./minute $\times 10^4$ .		E 40°/50° Calcs.
		40° C.	50° C.	
Silica alone . .	0·008	1·40	2·86	14,300
	0·013	3·00	5·50	12,200
	0·025	4·70	8·55	12,000
Glass alone . .	0·008	0·425	0·98	15,000
	0·013	1·06	2·175	14,300
	0·025	1·68	3·23	13,000
Dust alone . .	0·008	0·16	0·37	16,400
	0·013	0·33	0·70	15,100
	0·025	0·58	1·17	14,000

<sup>6</sup> B. H. Williams, *Trans. Faraday Soc.*, 24, 245 (1928).

TABLE VII.—CONCENTRATION OF HYDROGEN PEROXIDE = 1·5 NORMAL.

Nature of Surface.	(NaOH) Normality.	Initial Rate of Decomposition, g. $H_2O_2$ /c.c./minute $\times 10^{+4}$ .		
		40° C.	50° C.	60° C.
Silica . . .	0·008	0·915	2·03	4·10
	0·013	1·58	3·31	6·35
	0·025	3·50	7·02	12·60
Glass . . .	0·008	0·415	0·945	1·93
	0·013	0·83	1·785	3·55
	0·025	1·60	3·335	6·20
Wax . . .	0·008	0·115	0·27	—
	0·013	0·18	0·41	—
	0·025	0·40	0·85	—

TABLE VIII.—CONCENTRATION OF HYDROGEN PEROXIDE = 1·5 NORMAL.

Effect Due to:	(NaOH) Normality.	Initial Rate of Decomposition, g. $H_2O_2$ /c.c./minute $\times 10^{+4}$ .		E 40°/50° Cals.
		40° C.	50° C.	
Silica alone . .	0·008	0·80	1·76	15,900
	0·013	1·40	2·90	14,700
	0·025	3·10	6·17	13,800
Glass alone . .	0·008	0·30	0·675	16,200
	0·013	0·65	1·375	15,000
	0·025	1·20	4·85	14,600
Dust alone . .	0·008	0·115	0·27	17,100
	0·013	0·18	0·41	16,300
	0·025	0·40	0·85	15,000

### The Critical Increment.

The critical increments of the  $H_2O_2$  decomposition have been given in the tables. It is evident that in all cases the progressive addition of sodium hydroxide causes a lowering in the critical increment and at the same time a rise in the velocity of decomposition.

In the presence and in the absence of alkali, the critical increment increases with increase in initial concentration of  $H_2O_2$ . At the same time, the velocity of decomposition diminishes.

It is clear that the reaction takes place not only on the surface of the vessel, but also in the solution itself, both reactions (in the absence of alkali) having already been shown by F. O. Rice<sup>7</sup> and his collaborators, to be heterogeneous. The effect of the wall predominates over that in the bulk of the solution due to the dust and to the sodium hydroxide. That the effect ascribed to alkali is in fact due to this base and not to traces of ferric hydroxide is suggested by the results of the following section.

<sup>7</sup> F. O. Rice, *J. Amer. Chem. Soc.*, **48**, 2099 (1926); *J. physical Chem.*, **31**, 1507 (1927).

**The Effect of Ferric Hydroxide on the Decomposition of Hydrogen Peroxide in Absence and in Presence of Sodium Hydroxide.**

A great deal of work has been done on the influence of colloidal metals upon the decomposition of hydrogen peroxide in aqueous solutions, but only a little has been done on the influence of ferric salts on the decomposition of hydrogen peroxide, more particularly in alkaline medium. Bredig and Berneck<sup>8</sup> found the influence of iron oxide on the decomposition of hydrogen peroxide in alkaline solution to be negligible. In connection with the influence of ferric salts on the decomposition of hydrogen peroxide in acid medium, Bertalan<sup>9</sup> concluded that the velocity of reaction depends only on the total quantity of iron present. Johnson<sup>10</sup> found that ferric salts accelerate the decomposition of hydrogen peroxide and the reaction velocity decreases as the reaction proceeds owing to the hydrolysis of the catalyst. The addition of free acid was found to retard the reaction. Johnson and Robertson<sup>11</sup> showed the existence of an intermediate compound  $H_2FeO_4$  by spectroscopic examination of the reaction mixture. Duclaux<sup>12</sup> explained the variation of velocity constant by assuming the essential factors in this catalysis to be  $Fe^{+++}$  ions and the peroxide ions ( $HO_2^-$ ).

TABLE IX.

## 1. In absence of alkali.

Fe(OH) <sub>3</sub> , g. mol/litre.	Initial Rate of Decomposition, g. H <sub>2</sub> O <sub>2</sub> /c.c./minute $\times 10^4$ .	E. Cals.
0.00000	50° C.	0.610}
0.00000	40° C.	0.260}
0.00001	50° C.	1.60}
0.00001	40° C.	0.65}
0.0001	50° C.	4.40}
0.0001	40° C.	1.70}
0.001	50° C.	14.00}
0.001	40° C.	5.00}

## 2. In presence of alkali (0.05 N).

0.00000	50° C.	872}	12,000
0.00000	40° C.	479}	
0.00001	50° C.	855}	
0.00001	40° C.	470}	11,200
0.0001	50° C.	501}	
0.0001	40° C.	461}	11,000
0.001	50° C.	768}	
0.001	40° C.	450}	10,700

The work described in the present section was carried out with the purpose of studying the effect of traces of iron (which are inevitably present in metallic sodium) on the decomposition of hydrogen peroxide in neutral and alkaline media.

The *hydrogen peroxide* and the *sodium hydroxide* were prepared as in the previous section. The concentration of hydrogen peroxide (0.5*N* with

<sup>8</sup> Bredig and Berneck, *Z. physikal. Chem.*, 31, 258 (1899).

<sup>9</sup> Bertalan, *Z. physikal. Chem.*, 95, 328 (1920).

<sup>10</sup> Johnson, *J. physical Chem.*, 25, 19 (1921); *J. Amer. Chem. Soc.*, 45, 2512 (1923).

<sup>11</sup> Johnson and Robertson, *J. Amer. Chem. Soc.*, 45, 2493 (1923).

<sup>12</sup> Duclaux, *J. Chimie Phys.*, 20, 18 (1923).

respect to the mixture) and the concentration of sodium hydroxide ( $0.05\text{N}$  with respect to the mixture) were kept constant. The ferric hydroxide was freshly precipitated by adding sodium hydroxide to ferric chloride. The precipitate was carefully washed to remove any electrolyte and then dried in an air-oven at  $80^\circ\text{C}$ . for some hours. The concentration of ferric hydroxide with respect to the mixture was:  $0.00001M$ ,  $0.0001M$  and  $0.001M$ . Experiments were carried out at  $40^\circ\text{C}$ . and  $50^\circ\text{C}$ . in flasks freshly blown from glass boiling tubes and cleaned as described in the previous section.

The results are tabulated in Table IX. (p. 491) and the values recorded are the means of several concordant sets of measurements.

In the absence of alkali, the effect of ferric hydroxide on the decomposition of hydrogen peroxide may be due to the formation of an unstable basic peroxide of iron. There is also the possibility of ferric hydroxide giving rise to a surface effect just as in the case of dust.

In the presence of alkali, it is clear that the increasing addition of ferric hydroxide progressively lowers the rate of decomposition of hydrogen peroxide. There is, in this case, a complete reversal of the phenomenon occurring when ferric hydroxide is added to the solution in absence of alkali; that is to say, instead of accelerating the reaction in alkaline solution, ferric hydroxide retards the decomposition. Probably surface adsorption of sodium hydroxide on the ferric hydroxide first occurs. This may be followed by ferrate formation.

### Summary.

(1) The decomposition of hydrogen peroxide, in presence and in absence of sodium hydroxide, has been investigated in glass, wax, and silica vessels. The catalytic activity of the surface of the containing vessel and of the dust content of the solution, in each case, has been calculated. It was found that the order of magnitude of the catalytic activity of the vessels and dust was: silica > glass > wax (dust), in every case.

(2) The rate of decomposition decreases with increasing (initial) concentration of hydrogen peroxide.

(3) Increase of sodium hydroxide concentration causes an increase in the rate of decomposition.

(4) The critical increment increases with increasing initial concentration of hydrogen peroxide and decreases with increasing concentration of sodium hydroxide.

(5) The influence of small quantities of ferric hydroxide—such as might be present in caustic soda solutions—is shown to be negligible and consequently the positive catalytic effect attributed to hydroxyl ion is justified.

Part of the cost of this investigation has been borne by a grant made by Imperial Chemical Industries Ltd. to the Department of Physical Chemistry of the University of Liverpool which the writer acknowledges with gratitude.

The writer wishes to take this opportunity of expressing his thanks to Professor W. C. McC. Lewis, F.R.S., under whose supervision this work has been carried out.

## REVIEWS.

**History of Radio Telegraphy and Telephony.** By G. C. BLAKE, M.I.E.E., F.Inst.P. (London, 1928 : Chapman & Hall, Ltd. Pp. xix + 425.)

The volume is intended to appeal not only to those scientifically equipped for the study of the important subject of radio transmission and reception, but also to the vast throng of amateurs brought into being by broadcasting. It commences, therefore, with a foreword on the modern conception of electricity and its relation to matter and the ether.

The book is decidedly interesting as it gives an insight into several of the devices produced in the early days of this comparatively new science, when much of the so-called research consisted in setting out components on the laboratory table and connecting them up empirically to see what happened. One is inclined to feel that too much attention is devoted to such devices, but the author included them intentionally in the hope that new ideas might spring from these mostly forgotten schemes. It should be added that perusal of these early papers and patent specifications is important not only with a view to the evolution of new ideas but also to ascertain whether ideas are in fact new. Instances could be cited where apparently novel schemes are later found to have been included as subsidiary developments of early patent specifications which, as their main characteristics were improved out of recognition, lapsed and were forgotten.

This comparatively new branch of physics repays as fully as any other science the study of its history, and for this reason the volume is to be welcomed. It contains a mass of information, but unfortunately the index is not an adequate guide to its contents. The reviewer wished to verify the dates and individuals concerned with the inception of radio-telephony, with the first use of grid condensers and grid bias, with the development of means for securing selectivity and with the use of the three-electrode valve for high and for low frequency amplification. The index gave little help, and in fact the book itself did not always prove as helpful as was hoped. The book is in fact somewhat overloaded with the more bizarre of the old ideas to the detriment of a truly historical account of those which have stood the test of time and experience.

The book is printed throughout on art paper and consequently weighs nearly 3 lbs.; as nearly all the illustrations are line drawings a lighter paper might well have been used. The excellent collection of fifty pages of references to original papers and patent specifications might have been printed in a smaller type and thus have further lightened the physical labour of reading.

**The Theory of Emulsions and their Technical Treatment.** By WILLIAM CLAYTON, D.Sc., F.I.C. Second Edition. Pp. xi + 283. (London, 1928 : J. & A. Churchill. Price 15s. net.)

The study of emulsions has been very largely carried on in British and American laboratories, and it therefore seems appropriate—if unusual—that the first work dealing exclusively with this interesting and important class of disperse systems should be by an English author. The present edition contains over one hundred pages more than the first, which appeared in 1923 under the title “The Theory of Emulsions and Emulsification.”

All investigations of any importance appear to have been included in the present volume. A good deal of space is devoted to the subject of size-frequency distribution of particles ; the determination of which is gradually being recognised

as the only rational method of comparing the efficacy of different emulsifying agents or of different methods of agitation. Lecomte de Nouy's apparatus for determining interfacial tension is fully described ; this should be useful when the two phases have almost equal densities, as the drop number method then becomes inapplicable. The various theories of the structure of the interfacial layer—none of which, by the way, explains all the facts—are adequately summarised. A good account is given of the very puzzling results obtained by Seifriz, who finds that the density of a series of oils similar in all other respects determines the type of emulsion formed with the same emulsifying agents in identical working conditions.

In an appendix Professor Ramsden propounds a theory of emulsions stabilised by solid particles, a subject which has received intermittent attention, especially in connection with flotation processes, since Pickering first prepared emulsions with various inorganic precipitates as emulsifying agents. The theory is based on a theory of capillarity which has not yet been published in full, so that it is advisable to defer discussion.

A very complete bibliography filling twenty-four pages is a valuable feature of the work. The proof reader has done his work with care, but a somewhat puzzling description of the concentration of a sodium hydroxide solution as being "O. IN" has escaped him on page 134.

The volume is excellently printed and illustrated and can be thoroughly recommended to all students of disperse systems.

E. H.

**A Comprehensive Treatise on Inorganic and Theoretical Chemistry.** By J. W. MELLOR, D.Sc. Vol. VII. Ti, Zr, Hf, Th, Gt, Sn, Pb, Inert gases. ( $x + 977$  pp., 1927.) Vol. VIII. N, P. ( $x + 1110$  pp., 1928.) (London, Longmans Green & Co., Ltd. Price £3 3s. each volume.)

With the appearances of these two volumes, the number of the self-imposed labours successfully accomplished by our modern Hercules of Chemistry is brought to about sixty, and there now remain some twenty more to be tackled, viz., the transitional elements, the group V elements (except N and P), the group VI elements (except O) and manganese. Six previous volumes have afforded such ample opportunities for the expression of opinion as to the manner in which Dr. Mellor is carrying out his task that criticism in this field is hardly necessary, and now the main task of the reviewer is to indicate the scope of the new volumes as they appear.

In the title-page of Vol. VIII. we note with pleasure the first appearance after Dr. Mellor's name of the three letters indicative of the appreciation that his work has gained in the scientific world. Vol. VIII. is gracefully dedicated to "The Privates in the Great Army of Workers in Chemistry : their names have been forgotten : their work remains." A glance at the various volumes of this work makes one feel that one writer has done his best to assign credit to these Privates.

The pages allotted to the various elements are : Titanium, 97 ; Zirconium, 68 ; Hafnium, 7 ; Thorium, 80 ; Germanium, 21 ; Tin, 208 ; Lead, 467 ; Inert gases, 62 ; Nitrogen, 728 ; Phosphorus, 352. The account of hafnium is one of the first to appear in a systematic treatise, and the information accumulated since its discovery five years ago shows the intensity of modern research. Under thorium, seven pages are devoted to the Incandescent Mantle. A notable omission under tin is the failure to mention the resolution of this element. The discussion of the lead accumulator occupies five pages. The sections dealing with the uses and physiological action of lead include reference to lead tetraethyl. An annoying peculiarity of Dr. Mellor's arrangement of

matter is that, whereas metallic nitrates and phosphates may be found in the sections devoted to metals, nitrites, nitrides and phosphites are banished to Vol. VIII. It is a pity that the account of the inert gases has been added to Vol VII, as make weight.

The chemistry of nitrides has developed so as to need forty-seven pages. An interesting section deals with the analogies between liquid ammonia and water and a four-page table, giving the solubilities of an astonishing variety of substances in the former solvent, suggests that an extensive chemistry of reactions in this iron aqueous medium will arise. Sixteen pages are devoted to Ammines and Werner's Theory, but strangely the question of the optical activity of complex ions is entirely neglected.

The nitrogen cycle disturbs a poetic chord in Dr. Mellor for it causes him to break away from his normal terse style and write, "To-day a nitrogen atom may be throbbing in the cells of the meadow grass; to-morrow it may be pulsating through the tissues of a living animal . . ." And one cannot help parodying him by writing, "To-day a trivial chemical fact may be throbbing in the pages of an obscure journal; to-morrow it will most certainly be pulsating in the volumes of *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*."

C. H. S.

**Handbuch der anorganischen Chemie.** By R. ABEGG, F. AUERBACH und I. KOPPEL. Band IV, 3, Teil. i. Die Edelgase. Von Eugen Rabinowitsch. (8vo. Pp. xii + 522. Price: paper covers, 45 Marks; bound, 48 Marks. Hirzel, Leipzig, 1928.)

This, the latest volume of "Abegg" to appear, is the work of one author, and it has, therefore, been possible to deal with the whole group of inert gases on a uniform basis. The arrangement is founded on the conception of the structure of the atom, to which a study of these elements has contributed so much, and the volume also contains much independent information on this side, e.g., on the theory of spectra, which makes it useful apart from an interest in the inert gases. The author has aimed at including all the available information on the inert gases, covering their occurrence, separation, properties, and technical uses, so that the result is a valuable monograph with a very full collection of references to the literature. The volume well maintains the high standard of previous volumes of Abegg, and will be most useful both to chemists and to physicists. It is well printed on good paper, with fifty figures and 232 tables in the text.

J. R. P.

**Journal of the Electroplaters' and Depositors' Technical Society,** Vols. I. and II. (Price: Members, 8s. Non-members, 10s. London. The Electroplaters' and Depositors' Technical Society, Northampton Polytechnic Institute.)

The following papers are collected together:—

"Electrodeposition. A Survey of Modern Progress," by S. Field. "A General Survey of Chromium Plating," by E. A. Ollard. "Metal Cleaners in use in electroplating," by E. J. Dobbs. "Heavy and Rapid Deposition," by J. S. Sunderland. "Addition Agents in Electrodeposition," by S. Wernick. "Deposition of Cadmium," by E. J. Dobbs. "Nickel Plating Solutions. Their Composition and Properties," by E. A. Ollard. "The Commercial Deposition of Nickel," by E. J. Dobbs. "The Acidity of Certain Electroplating Solutions," by

A. W. Hothersall. "Electrodeposited Coatings for Prevention of Corrosion," by H. Sutton. "Electrodeposition of Iron," by T. Johnson. "The Protective Effects of Metal Deposits on Iron," by S. Wernick. "Electrolytic Silver Refining," by E. Downs.

The volume under review comprises a collection of the papers read before the Society during the sessions 1925-26 and 1926-27, and provides ample evidence that the Society has made a good start on its useful career. As a protégé of the Faraday Society the young Society has our best wishes for continued success.

**Atomic Structure as Modified by Oxidation and Reduction.** By W. C. REYNOLDS, D.Sc. (LOND.), F.I.C., A.R.C.S. Pp. viii and 128. (London : Longmans, Green & Co., Ltd. 7s. 6d. net.)

The character of Dr. Reynolds' book on "Atomic Structure as Modified by Oxidation and Reduction" can be judged from a paragraph on page 2, in which he states that "The present spectroscopic classification of these electrons is unsuitable for chemical discussion, and it is probable that it will undergo drastic modification before long. It is the physical counterpart of the artificial Linnæan classification in botany, and, like the latter, must ultimately for most purposes be discarded in favour of a natural system, when the science is sufficiently developed. For the present purpose, therefore, a purely chemical arrangement has been adopted." In this chemical arrangement, electrons are grouped in three classes as follows :—

- I. The valence electrons.
- II. The potential valence electrons.
- III. The radial quartets and pairs.

He adds that : "At present the majority may be regarded as rotating in pairs or quartets about a few symmetrically placed centres *outside* the nucleus. Electrons moving in planetary fashion around central nuclei, or in cassinian curves about two, have yet to justify chemical consideration." From this statement it appears that the author's electrons have none of the properties of real electrons, and are purely imaginary quantities to which hypothetical, physical and chemical properties are assigned. In particular, whilst the rotation of electrons about a positive nucleus is a phenomenon which still has a plausible physical basis, in spite of the advent of the wave theory, there is no imaginable process which would justify the assumption that pairs or quartets of electrons can revolve indefinitely round a hypothetical point in space which contains no positive charge. The greater part of the author's conclusions can be deduced from an electronic theory of valency which is in harmony with physical facts. In the opinion of the reviewer, therefore, the publication of a book in which physical facts are ignored is a real disservice to chemistry, since it provides some justification for the unkind suggestion that chemical theories of valency are determined even more by the author's ignorance of physics than by his knowledge of his own science.

T. M. L.

## THE CAUSES AND PREVENTION OF PITTING IN ELECTRODEPOSITED NICKEL.

By D. J. MACNAUGHTAN AND A. W. HOTHERSALL.\*

*Received 25th July, 1928.*

### Introduction.

The following is an account of the first part of a general investigation upon the causes and prevention of pitting in electrodeposited nickel, carried out in the Research Department, Woolwich, for the Electrodeposition Committee of the Department of Scientific and Industrial Research. This portion of the work is particularly confined to a study of the appearance of the defect, the manner of its occurrence and the relation between pitting and surface imperfections in the basis metal. It is prefaced by a short survey of previously published information on the subject and a bibliography is appended.

### PART I.—SURVEY OF LITERATURE.

The defect known as pitting not infrequently occurs in the electrodeposition of the base metals, iron, nickel, cobalt, and zinc, but only rarely occurs in the electrodeposition of the more noble metals, copper and silver.

The presence of pits in thin deposits of nickel seriously diminishes their decorative and protective value. In thick deposits of this metal which are being increasingly used for engineering purposes, such as the building up of worn or undersized parts, the presence of the defect results in inferior static and dynamic mechanical properties. The value of electro-formed nickel deposits, such as electro-types, tubes and sheet, may be destroyed by the presence of a single pit.

### Description of the Defect.

Various investigators<sup>1, 2, 3, 4, 5</sup> have referred to the occurrence of pitting as a frequent cause of trouble in the electrodeposition of nickel. No complete description of the defect, however, appears to have been published, although references to its character have been made.<sup>1, 4, 6, 7, 8</sup> Usually the defect is described as consisting of small crater-like depressions which may be present in thin or in thick deposits, and may, or may not, penetrate through to the basis metal. Occasionally, however, the defect is described<sup>1, 6</sup> as consisting of small holes in the deposit and is referred to as "pinholing." This alternative description of the defect is liable to cause confusion. Thus if thin deposits of nickel are stripped from the cathode when only a few ten thousandths of an inch in thickness, and examined by transmitted light they are usually found to be perforated with numbers of fine holes, such as might be formed by perforation by a pin.<sup>9</sup> These holes might be quite justifiably termed pinholes, but are generally described as

\* Communication from the Research Department, Woolwich.

pores. They differ markedly from pits. They diminish in size and number as the deposit is increased in thickness and in general mostly disappear, by closing up, when the deposit has reached a thickness approximating to one thousandth of an inch. Pits on the contrary frequently increase considerably in dimensions as the thickness of the deposit is increased.

The presence of pinholes or pores in a deposit necessarily involves porosity in amount proportional to their number and size.<sup>10, 11</sup> On the other hand the presence of pits does not necessarily involve porosity, in view of the fact that pits, as distinct from pinholes, or pores, may not extend in depth to the basis metal.<sup>12, 13</sup> A connection between pitting and porosity may nevertheless exist.<sup>14</sup>

### The Immediate Cause of Pitting.

In order to cause the formation of a pit or small crater in a deposit some factor or factors must operate to cause a partial screening of the surface from the depositing current at the site of the defect, thereby producing a local decrease in the amount of metal deposited.

There are two screening agencies liable to occur at the cathode surface, *viz.*, (a) solid particles such as graphite or nickel from the anode slimes, or ferric hydroxide precipitated from the solution; (b) bubbles of gas.

*Solid Particles.*—In general, it has been found that solid particles are more likely to produce growths, than pits, on a deposit.

*Bubbles of Gas.*—Pits are usually caused by bubbles of gas formed at the cathode surface. The gas causing the defect may be air, oxygen, or hydrogen. Air may be present as a result of being dissolved from the atmosphere at one temperature and liberated owing to diminished solubility at a higher temperature. Oxygen may be produced at the anodes, and some of this gas may subsequently be liberated at the cathode surface. Hydrogen is likely to be present as a result of the discharge of hydrogen ions. Each of these gases has been suspected of being a chief cause of the defect.

*Nature of the Gas.*—(i) *Air.*—Burgess and Watts<sup>15</sup> and later Watts<sup>16</sup> have expressed the view that air bubbles are an important cause of pitting. Their opinions were based upon the evidence they obtained that the defect is liable to be particularly produced under conditions that favour air absorption by the solution; and that, in such cases, boiling the solution, which would remove the air, eliminates the defect. No confirmation of their view by analysis of the gas evolved has been recorded.

(ii) *Oxygen.*—The suggestion that oxygen produced at the anode and subsequently discharged at the cathode is an important cause of pitting<sup>8</sup> would connect the defect with such conditions as produce passivity at the anodes and thereby cause discharge of oxygen. No experimental evidence has been recorded which supports this view. Madsen,<sup>4</sup> however, in indicating the conditions necessary for the avoidance of this defect in nickel deposits emphasises the importance of using anodes of such a composition as to be free from any tendency to passivity.

(iii) *Hydrogen.*—For the nickel plating solutions ordinarily used, it is not possible to predict, from the equilibrium potential of nickel and hydrogen, the ratio in which these elements are liable to be deposited, owing to the uncertain value of the polarisation of nickel and of the over-voltage of hydrogen. Under the most carefully regulated conditions, current efficiencies in nickel deposition approach closely, but do not actually reach 100 per cent. Some hydrogen is therefore always deposited

with the nickel and this gas, more than any other, has been regarded as the chief cause of pitting in nickel deposits.

### **Further Consideration of Hydrogen as a Cause of Pitting.**

*1. Influence of the Acidity of the Electrolyte.*—Upon the assumption that hydrogen gas bubbles are likely to cause pitting, it has been frequently recommended that, in order to avoid this defect, the conditions of deposition should be adjusted so as to secure the minimum discharge of this gas, and, to this end, the acidity of the solution used should be kept as low as possible.<sup>1, 8, 15</sup>

Also it has appeared that, apart from the influence of the acidity of the solution upon the quantity of hydrogen discharged, there is a further effect it may produce upon the adhesion of the bubbles of gas to the cathode.

Townsend<sup>17</sup> and then Newbery<sup>18</sup> showed that electrolytically produced gases are frequently electrically charged. Coehn<sup>19</sup> subsequently found that hydrogen bubbles formed at a cathode in an alkaline solution are negatively charged and in consequence are electrostatically repelled by the negative cathode, but in acid solutions they are positively charged and therefore are attracted by the cathode. In the former case the electrostatic attraction is opposed to, and in the latter case added to, the capillary forces normally operating to cause the bubble to cling to the cathode surface. If these conditions hold for nickel plating solutions, it might be anticipated that increased acidity, within the range permissible for nickel deposition, would not only favour increased hydrogen discharge but would also increase the tendency of the bubbles to adhere to the cathode surface.

Thompson<sup>20</sup> and subsequently Montillon and Cassel<sup>21</sup> studied the influence of acidity upon the appearance of nickel deposits obtained from various nickel plating solutions and concluded that the  $\rho_H$  range 3-4 favours pitting whereas the  $\rho_H$  range 5.5-6.5 inhibits the defect. On the other hand Foerster and Krüger<sup>22</sup> found pitting to be more prevalent in the range above  $\rho_H$  5.5. Recent plating experience has indicated that even with careful control of the acidity within close limits the defect may occur at one time and not another.<sup>5, 23</sup> It would thus appear that no conclusive evidence connecting high acidity and pitting has been established.

Even the total absence of any direct relationship between the acidity of the solution and the occurrence of the defect does not however exclude the possibility of hydrogen bubbles being the immediate cause of the defect. Variations in other conditions than the acidity may affect the overvoltage of hydrogen at the cathode and thereby cause corresponding changes in the total amount of hydrogen discharged and possibly variously affect the rates of hydrogen discharge at different points over the surface of the cathode. There is the further possibility that the actual degree of adhesion of the bubbles may be modified from time to time as a result of the influence of certain factors not directly connected with the acidity of the solution.

### **(2) Effect of Impurities upon Hydrogen Overvoltage and on Pitting.**

In the electrodeposition of zinc from an acid solution it has been found that pitting of the deposit is liable to occur if certain impurities are originally present at, or are subsequently deposited upon, the cathode.<sup>24</sup> The defect appears to be caused by local decreases of hydrogen overvoltage at the sites of the impurities. In nickel deposition the effect of such impuri-

ties is not likely to be so pronounced and has not been definitely established although it has been strongly suspected.<sup>4</sup>

### (3) Influence of the Nature of the Cathode Surface.

The overvoltage of hydrogen tends to be less upon a roughened than upon a smooth surface so that variation in the nature of the surface of a cathode is liable to produce local differences in the amount of hydrogen discharged during deposition. Differences in the nature or degree of the chemical etching of the cathode prior to deposition would tend to cause corresponding variations in the discharge of hydrogen at the surface. Such variations would be particularly liable to occur if there were present at the cathode surface impurities more susceptible to attack by the etching reagent than the rest of the cathode. Local differences in hydrogen overvoltage may also arise as a result of certain impurities, such as particles of nickel, graphite or iron hydroxide, settling upon the cathode surface.

### (4) Influence of Capillary Forces at the Cathode.

The surface tension of the electrolyte and the interfacial tension between the electrode and the electrolyte largely determine the concentration of molecular hydrogen that is necessary to generate a bubble of the gas at the surface of the cathode and the force necessary to secure its final detachment. The influence of these capillary forces is greatly modified by the temperature, the composition of solution, and the nature of the electrode. In considering the elusive nature of pitting, it is, however, only necessary to regard the possible variations in their effect that may arise during deposition in a nickel-plating solution of constant composition, maintained at a uniform temperature, and at a fixed  $p_H$  and current density.

Variations may arise from the presence in the solution of (a) colloidal matter, which is liable to affect both the surface tension of the electrolyte and the interfacial tension between the electrode and the electrolyte, and (b) the presence of oily or greasy matter, which if concentrated at the cathode surface would modify the interfacial tension between the electrode and electrolyte.

(a) *The Effect of Colloidal Matter.*—Some form of organic matter is frequently present in nickel plating solutions. Apart from its possible introduction as an impurity in the salts used, it may be formed as an oxidation product of the carbon present as carbide or graphite in the anodes. It may also be introduced from the air in the form of dust or organic spores; certain fungi propagate in nickel plating solutions. Various investigators<sup>4, 6</sup> regard such organic material as a source of colloidal impurities which are considered to become an important cause of pitting in nickel deposits.

No positive evidence has however been put forward that clearly establishes the assumed connection between the defect and the presence of colloidal matter. On the contrary, in zinc deposition it has been found that the addition to the solution of an organic colloid such as gelatine causes the bubbles of hydrogen formed during deposition to detach themselves more readily from the cathode surface so that there is a decreased tendency to the formation of pitted deposits. The effect may be in part at least accounted for by an observed decrease in the surface tension of the electrolyte and a decrease in the interfacial tension between the electrode and electrolyte;<sup>24, 25</sup> it is also possible that the decreased adhesion of the bubbles may be due in some measure to an effect of the colloid upon the bubble charge.<sup>27</sup>



$\times 12$

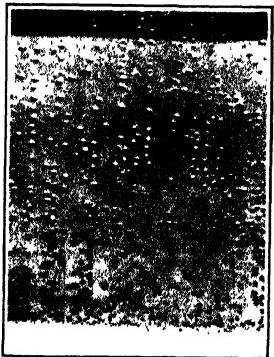
FIG. 1.—Cross-section through closed pit in nickel deposit.  
0·18 in. thick.

Copper deposit. Nickel deposit. Steel.



$\times 25$

FIG. 2.—Cross-section through pit in nickel deposit above defect in underlying steel.



$\times \frac{1}{2}$

FIG. 3.—Circular pits in nickel deposit.  
0·02 in. thick.



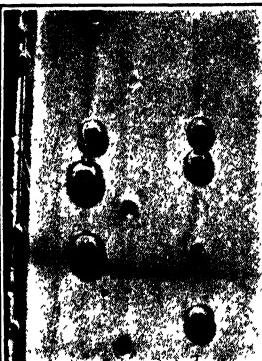
$\times \frac{1}{2}$

FIG. 4.—Tailed pits in nickel deposit.  
0·02 in. thick.



$\times \frac{1}{2}$

FIG. 5.—Pits in nickel deposit, 0·02 in. thick, showing distribution along surface defects in basis metal.



$\times 5$

FIG. 6.—Pits in nickel deposit during deposition, revealed by dislodgment of gas bubbles.

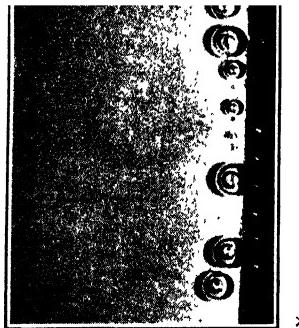


FIG. 7.—Cathode during nickel deposition showing bubbles above surface defect in underlying steel.



FIG. 8.—Cathode during nickel deposition showing bubbles above surface defect in underlying brass.

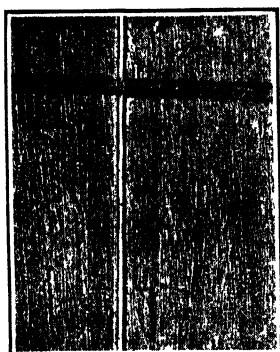


FIG. 9.—Copper-plated steel cathode during nickel deposition. Thickness of underlying copper, .001 in.

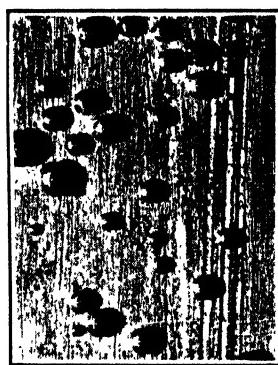
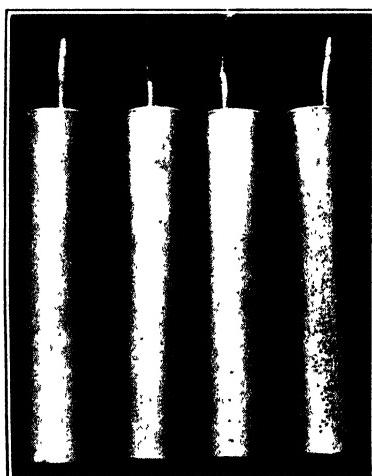


FIG. 10.—Copper-plated steel cathode during nickel deposition. Thickness of underlying copper, .00015 in.



FIG. 11.—Nickel deposit, 0.02 in. thick, upon bright rolled steel rod, showing formation of pits on surface defects.



No. 1.    No. 2.    No. 3.    No. 4.  
FIG. 12.—Nickel deposits, 0.01 in. thick, showing "basis metal pitting" and "solution pitting."  
No. 1.—Coppered steel    No pits.  
" 2.—Steel                 Basis metal pitting.  
" 3.—Coppered steel      Solution pitting.  
" 4.—Steel                 Basis metal and solution pitting.

In view of results obtained in zinc deposition it appears justifiable to doubt the correctness of the assumption that organic colloidal matter is an important cause of pitting in nickel deposition. On the other hand while colloidal matter in general appears likely to reduce the surface forces so that bubble adhesion is diminished, such matter would also have the effect of increasing the viscosity of the solution and this may have a contrary effect upon bubble separation. Any marked increase in viscosity would tend to diminish the speed with which the buoyancy of the bubbles carries them to the surface. If this decrease in speed is considerable it might result in the imprisonment of bubbles in the growing deposit.<sup>23</sup> Only the presence of large amounts of colloidal matter is likely to have any considerable effect in this way, and it is improbable that the amount of colloidal matter present in a nickel-plating solution would be adequate to cause this effect.

(b) *The Effect of Matter of a Greasy or Oily Nature.*—The presence of any matter of an oily or greasy nature on the cathode due to imperfect cleaning or arising from a contaminated bath would tend markedly to increase the interfacial tension between the cathode and the electrolyte. This would result in an increased adhesion of bubbles of hydrogen to the cathode surface and would thus tend to cause pitting of the deposit.<sup>24</sup>

## PART II.—PITTING IN DEPOSITS AND ITS RELATION TO SURFACE DEFECTS IN THE BASIS METAL.

### Description of the Defect.

In the course of the investigations on the causes of pitting, a considerable number of deposits of nickel and a smaller number of deposits of iron, cobalt, zinc and copper have been prepared. In the deposits of each of these metals some examples of pitting have been obtained. Examination of the defect in these examples has shown that nearly all pits may be placed in one of two groups, *viz.* : (1) circular pits, (2) tailed pits.

*Circular Pits.*—These consist of almost perfectly round depressions in the deposit which in thin coatings of nickel such as are formed for decorative purposes appear as bright dots. A circular pit may occur with a bright mirror-like or a dull interior surface. Evidence has been obtained which indicates that the latter are pits which have commenced to heal up by deposition of metal over their interiors. When this takes place, progressive contraction in diameter of the pit tends to occur owing to preferential deposition of metal at the rim, and if deposition is continued for a sufficient length of time, the pit may close up entirely. Fig. 1 illustrates a section through a completely closed-up pit in a nickel deposit.

Viewed in cross-section pits of both the circular and the tailed variety frequently but not invariably extend through the whole depth of the deposit, and thus appear to have commenced to form at the beginning of deposition. (See Fig. 2.)

Fig. 3 shows a number of typical circular pits in a nickel deposit upon a steel cathode.

*Tailed Pits.*—A pit of this group, viewed with the cathode placed in the same vertical sense as that in which it was plated, consists of a more or less circular depression, the upper edge of which merges into an extension or tail oriented in a direction approximately at right angles to the surface of the depositing solution. The combined contour of the depression is thus comet shaped. In some cases the extension above the main depression consists in a narrow groove in the deposit which diminishes

in depth as it proceeds from the depression until it becomes a mere streak. Typical examples of tailed pits are shown in Fig. 4.

As in circular pits, the interiors of tailed pits are usually brighter than the surrounding deposit and when the interior is dull, evidence has shown that the pit has commenced to heal up.

Other types of pit which have been less frequently observed are:—

(1) Circular pits having outgrowing rims, the growth of metal at the rim in certain cases being such as to form an almost complete dome-like covering over the pit. This type of pit has been particularly observed in nickel deposits produced in solutions containing citric acid.

(2) Annular pits which have formed around a projection as a result of local deviation of current to the growing surfaces of the projection. This type of pit has not been found to occur to any marked extent in deposits of nickel or iron.

(3) Conical depressions caused by the forcible uprooting of growths present in a deposit during machining or polishing after deposition.

*Pits in Deposits of Iron, Cobalt, Zinc, and Copper.*—Examination of a considerable number of deposits of iron and cobalt and a lesser number of deposits of zinc has shown that the pits that occur in deposits of these metals are similar in form and dimensions to those that occur in nickel deposits. The presence of pits in copper deposits is rare. When they do occur, the conditions of deposition are generally abnormal. Conical cavities due to growths which have been broken away from the deposit are more frequent than normal pits in deposits of this metal.

*Distribution of Pits.*—Pits sometimes occur irregularly distributed in an apparently haphazard manner over a cathode with a preference for the under surfaces and edges of the cathode when this is considered in relation to its position in the deposition bath. They may also occur grouped over a deposit in some sort of order, e.g., regimented in rows as shown in Fig. 5. Not infrequently, irregular and regular distribution of pits occur simultaneously on the same deposit.

#### Examination of the Cathode during Deposition.

By means of the apparatus shown in Fig. 13 a magnified image of the illuminated portion of the cathode surface was viewed on a ground glass screen at S. The method used for circulating, heating and filtering the electrolyte is shown diagrammatically in Fig. 14.

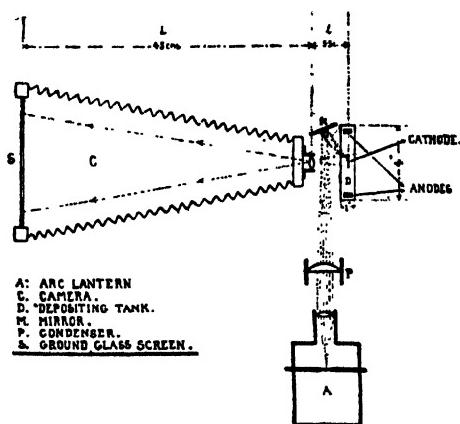


FIG. 13.—Examination of cathode during deposition.

The nickel anodes and the nickel sulphate used for preparing the depositing solutions were specially purified in the manner recently described by the authors,<sup>28</sup> and had the composition shown in Table I. For the other constituents of the depositing solutions, materials of A.R. purity were used.

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TABLE I.

## COMPOSITION OF REFINED NICKEL ANODES AND PURIFIED NICKEL SULPHATE.

	Carbon Per Cent.	Iron Per Cent.	Copper Per Cent.	Manganese Per Cent.	Zinc Per Cent.	Lead Per Cent.	Silicon Per Cent.
Refined nickel anodes .	nil	.0015	.001	.0004	trace	trace	nil
Purified nickel sulphate .	—	<.005	<.001	.001	trace	<.005	—

*Observations on the Formation of Pits.*—A large number of experiments were carried out in which the cathode was observed in the apparatus described. In all cases pits were found to be produced either when bubbles of gas clung to the cathode for prolonged periods during deposition or by a succession of bubbles proceeding from a particular point on the cathode surface. In the former case, if adhering bubbles were dislodged from the surface by tapping the cathode the underlying pits were revealed. An example is shown in Fig. 6.

A pit exposed in this way by the discharge of, or forcible removal of, its bubble invariably showed a bright interior surface. If no fresh bubble formed in the pit, the interior lost its brightness after a time owing to the deposition of nickel inside.

*Formation of Tailed Pits.*—Observations of the formation of tailed pits made in the apparatus described supplemented by evidence obtained from experiments carried out in ordinary deposition tanks indicated that the formation of tailed pits was connected with the upward flow of the electrolyte over the cathode surface.

The depletion of metal ions from the film of electrolyte in contact with the cathode, which occurs during deposition, renders it less dense than the surrounding liquid so that it rises to the surface of the solution. A circulation is thereby set up which causes fresh solution to flow towards the cathode bringing its supply of metal ions. In a non-agitated bath, apart from the effect of thermal convection currents, the supply of metal ions to the cathode surface thus secured is much greater than that due to the migration of metal ions under the influence of electrostatic attraction to the cathode. In consequence, in non-agitated solutions the rates of deposition used are dependent upon the upward flow of electrolyte induced by the changes in density that occur.

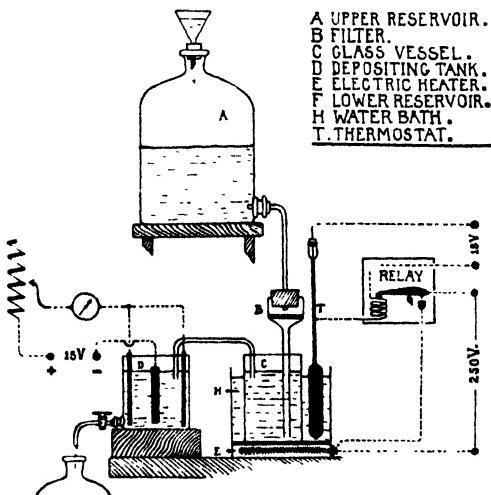


FIG. 14.—Examination of cathode during deposition.

It is to be anticipated therefore that any influences that retard the upward flow are liable to affect the conditions of deposition. Thus immediately above a bubble clinging to the cathode surface, local stagnation of the electrolyte with consequent depletion in metallic ions is liable to occur. This will tend to cause a marked decrease in the amount of nickel deposited, thereby producing immediately above the bubble a depression, the depth of which will in general, decrease rapidly as the distance from the bubble increases, until it is no longer perceptible as a depression. The lessened effect of the obstruction may, however, still continue as a streak.

The degree of obstruction exerted by a bubble on the up-flowing cathode liquid will be affected by its position in relation to the cathode stream. Thus it has been found that when the cathode is horizontal, little or no obstruction occurs and the shape of the pits tends to be circular, while if the cathode is hung vertically, the degree of obstruction is at a maximum and tailed pits are more likely to be formed.

Similarly it has been observed that circular pits more frequently occur on vertical surfaces when the electrolyte is highly concentrated in respect to metallic ions. In such cases, at the ordinary rates of deposition, the percentage depletion of metallic ions at the cathode surface is smaller than in less concentrated solutions, so that the change in density, which affects the rate of upward flow of the solution, is less.

*The Bright Mirror-like Interior of Pits.*—Artificially produced pits having mirror bright interiors and bright streaks arising from their upper edges were formed by nickel deposition upon a cathode on to which was sprung a glass clip made of thin glass rod bent into an O shape, the two ends of the rod terminating in glass beads. These artificially formed pits which were due to the screening effect of the glass beads bore a strong resemblance to pits formed by gas bubbles and indicated that the brightness of the interior of a pit is solely a result of screening.

The effect of screening a portion of the cathode surface is chiefly to (1) diminish the current density; (2) cause local stagnation of the electrolyte. With reference to (1), experiments showed that when the cathode current density in nickel deposition is reduced to a low value the deposit takes on a brighter appearance and the current efficiency falls off, the amount of hydrogen discharged relative to nickel increasing. With reference to (2) it was noted that a deposit of nickel hydroxide was formed at the bases of a number of pits in thick nickel deposits. To what extent, if at all, the brightness of the interior of the pits is due to the co-deposition of hydrogen in a thin layer of nickel or due to the precipitation of nickel hydroxide has not yet been ascertained. Both of these factors may operate to reduce the crystal size of the deposit, thereby increasing its brightness.

### Consideration of Pitting in Relation to Surface Defects.

Experiments carried out to determine the effect of replacing commercial nickel anodes and salts with the purified materials already referred to showed that while pitting was not eliminated by the use of purified materials, it was reduced in amount and appeared to be confined to areas of the cathode that were suspected to contain surface defects.

Some typical experiments in which the surfaces of the cathodes were kept under observation in the apparatus described were as follows:—

*Conditions of Deposition.*—The solution contained 240 gms. purified nickel sulphate, 30 gms. A.R. boric acid, 19 gms. A.R. potassium chloride per litre. Nickel anodes of high purity prepared as previously described

were used. Temperature  $35^{\circ}\text{C.} \pm 2^{\circ}$ ,  $p_{\text{H}} 5.8-6.1$ , current density 15 amperes per sq. foot.

(a) *Deposits on Mild Steel Strip.*—The strip was stopped off on the edges and upon one face with collodion varnish and was then subjected to cathodic cleaning in an alkaline solution followed by anodic cleaning in 25 per cent. sulphuric acid (by weight) after which it was washed and placed in the depositing vessel and clamped with its uncovered metal surface facing the camera.

During the first 20 minutes of deposition bubbles were constantly being discharged and reformed at points along surface defects in the mild steel. After a time this process became slower the discharge of bubbles finally ceasing. At some places a large bubble was left adhering to the cathode. At other places after the discharge of a bubble no further bubble formed at the same point and the pit commenced to heal up.

Upon removal of the deposit from the bath the pits were found to be grouped along the surface defects. Fig. 7 shows a portion of the surface after three hours' deposition when the deposit was approximately '0025 inches thick. The bubbles are grouped above a surface defect in the steel.

(b) *Deposits on Brass.*—The preparation of brass strip for deposition involved removal of grease in an alkaline solution and removal of oxide by immersion in nitric acid (1.2 S.G.). The conditions of deposition were similar to those used for mild steel strip. Gas bubbles were formed at defects and behaved similarly to those at defects in mild steel strip as described already. Fig. 8 shows bubbles clinging to the surface of the cathode above a spill in the underlying brass.

(c) *Deposits on Copper.*—Similar results to those obtained with mild steel strip and brass were obtained with rolled copper sheets containing inclusions, pitting taking place in the defective areas.

Some experiments were made with copper sheets, the surfaces of which were first ground and polished and then cleaned in the same manner as the brass strip. With the conditions of deposition used previously, it was found that no bubbles of gas whatever formed on the surfaces of these cathodes during deposition and the deposits were entirely free from pits.

Experiments were subsequently made to ascertain whether an electro-deposited layer of copper formed on the surfaces of the rolled copper sheets prior to nickelling would eliminate pitting by covering up the surface defects. The deposit of copper was formed in an acid copper sulphate solution the preparation of the copper sheet being the same as for nickelling. The nickel deposits produced on the treated copper sheets were free from pits. Observations made during deposition showed that no bubbles were evolved at the surface of the copper coated cathodes.

#### **Elimination of Pitting at Surface Defects in Steel by a Preliminary Coating of Copper.**

The elimination of pitting on surface defects in rolled copper sheets by a preliminary coating of electrodeposited copper suggested that a similar treatment of steel surfaces might prove equally beneficial.

It is not possible to deposit copper directly on steel from the acid copper sulphate solution, as in this solution a steel surface is instantly attacked and covered with a layer of precipitated copper which prevents satisfactory adhesion of subsequently deposited copper. The steel may, however, be coated directly with electrodeposited copper from a copper

cyanide solution or it may be given a preliminary thin coating of electrodeposited nickel and then a coat of copper deposited from the acid copper sulphate solution. The latter method was found to be more convenient and was adopted.

Samples of cold rolled mild steel which showed surface defects were coated with nickel for thirty minutes at 15 amperes per sq. foot and then with copper at the same current density for periods varying from ten minutes to three hours. They were then plated with nickel, the cathode surface being kept under observation.

It was found that a deposit of more than 0.0003 inches of copper (twenty minutes' copper deposition at 15 amperes per square foot) was sufficient to prevent the formation of bubbles at the surface defects and eliminated pitting.

The effectiveness of the treatment with copper is shown in Figs. 9 and 10 which were obtained after ten minutes' deposition on steel cathodes which had previously received preliminary copper coatings 0.001 inches and 0.00015 inches in thickness respectively (produced by seventy minutes and ten minutes' copper deposition at fifteen amperes per square foot).

*Hydrogen Overvoltage and Pitting.*—With a view to confirming that the beneficial effect of a copper deposit on steel in eliminating pitting during subsequent nickel deposition was due to the suppression of hydrogen discharge, tests were carried out to compare the cathode efficiencies of nickel deposition upon cathodes of cold rolled mild steel containing surface defects and of the same material coated with electrodeposited copper. The duration of each test was fifteen minutes. The average of seven tests upon the steel surface gave a metal efficiency of 98.0 per cent., while six tests upon the copper surface gave an average of 99.1 per cent. metal efficiency. These results indicate that an appreciably greater amount of hydrogen is discharged at the steel surface than at the copper surface, and suggests that the gas bubbles which formed at surface defects during nickel deposition upon steel cathodes in the experiments previously described were partly if not wholly composed of hydrogen.

Preferential discharge of hydrogen at surface defects suggests decreased hydrogen overvoltage at these defects relative to the hydrogen overvoltage elsewhere on the cathode surface. This is in accordance with the indications of other investigations referred to in Part I.

If the postulated connection between overvoltage and pitting is correct the beneficial effect of copper would appear to consist not only in covering up these defects and thereby eliminating these areas of lower overvoltage but also in providing a basis metal for nickel deposition upon which overvoltage of hydrogen discharge is higher than upon steel.

*Solubility of Hydrogen in Nickel-Plating Solutions.*—The fact that no bubbles at all were observed to form during nickel deposition upon copper deposits of suitable thickness, although the efficiency tests suggest that a small discharge of hydrogen does occur, requires some explanation. The discrepancy may be accounted for by the solubility of hydrogen in the nickel-plating solution used. According to Winkler,<sup>29</sup> one litre of water at 35° C. will dissolve 15.74 c.c.s of hydrogen measured at 0° C. and 760 mm. pressure. Measurements of the solubility of hydrogen in a nickel-plating solution containing 120 gms. nickel sulphate, 21 gms. ammonium sulphate, and 8 gms. potassium chloride indicated that one litre of the solution at 35° C. would dissolve approximately 9 c.c.s of hydrogen measured at 0° C. and 760 mm. pressure.

In view of the not inconsiderable solubility of hydrogen in the nickel

depositing solution it would appear possible for hydrogen to be dissolved at the cathode surface without first appearing in the form of bubbles. This may explain the discrepancy between the observations made of the appearance of the copper cathode surface and the results of the efficiency tests on a similar surface.

### **"Basis Metal Pitting" in Nickel Plating. Solutions of Commercial Purity.**

The results of the experiments with highly pure material emphasised the influence of the nature of the basis metal on pitting. Experiments carried out with commercial salts and anodes were confirmatory.

Fig. 11 shows the effect of machining a bright rolled steel bar which was found to give rise to pronounced pitting of deposited nickel owing to the presence of oxide rolled into the surface.

Pitting caused by defects in steel could be eliminated with greater certainty than by machining by giving a preliminary copper coating on top of a thin coating of nickel in the manner previously described. A thickness of copper approximately .0004 inches was suitable for this purpose.

*"Basis Metal Pitting," and "Solution Pitting."*—Using commercial salts and anodes it was found that even when all precautions had been taken to avoid basis metal pitting by treatment with copper in the manner described, pitting was not invariably eliminated although it was frequently reduced.

The other conditions causing pitting appear to arise from a defective condition of the solution. Pitting arising solely from these conditions will be subsequently referred to as "solution pitting."

The possibility of eliminating basis metal pitting on a cathode by means of a deposit of copper of suitable thickness makes it practicable to ascertain when a particular nickel-plating solution is giving rise to solution pitting.

The following is an example of the use of this method extended, however, to show both basis metal and solution pitting.

Pitted deposits had been frequently obtained from a particular solution A and only occasionally from another solution B of similar composition. Tests were made to ascertain to what extent the occurrence of the defect was due to the condition of the solution.

Four lengths of steel were obtained from a bar which was found to have oxide inclusions at the surface. Two of these lengths were given a thin deposit of nickel followed by a layer of copper .005 inch in thickness. One of these bars, No. 2, was introduced into solution A and the other, No. 1, into solution B and nickel deposited in each case at a current density of 15 amperes per square foot,  $\rho_H$  5.8. Temperature 35°. Time of deposition, 12 hours.

Upon removal from the bath the deposit from solution A was found to be pitted whereas that from solution B was free from the defect. It was evident that solution A was giving rise to solution pitting whereas solution B was not.

The difference between solution pitting and basis metal pitting was shown by simultaneously nickelplating the two remaining bars, cleaned but not coppered, one in each solution. The deposit from solution B on bar No. 3 showed basis metal pitting and the deposit from solution A on bar No. 4 basis metal pitting, together with solution pitting. The four deposits are shown in Fig. 12.

**Previously Recommended Use of an Intermediate Layer of Electrodeposited Copper to Reduce Porosity in Nickel Deposits.**

The process of coating a steel article first with nickel, then with a thick deposit of copper and finally with a deposit of nickel has been previously recommended for the reduction of porosity in nickel deposits in order to secure a corresponding increase in resistance to corrosion. See Langbein and Brann,<sup>30</sup> E. M. Baker,<sup>31</sup> M. Schlotter,<sup>10</sup> Thomas and Blum.<sup>11</sup>

The beneficial effect of this procedure in reducing pitting, as distinct from porosity, does not appear to have been so definitely recognised, probably owing to the frequency with which solution pitting may occur in deposits that have been treated in this manner.

The results of the investigations described have indicated the beneficial effect of the intermediate deposit of copper in the elimination of pitting arising from defects in the basis metal.

It will further be shown in subsequent reports that the possibility thus created of distinguishing basis metal pitting is a valuable preliminary step in ascertaining the nature of the other factors operating to produce solution pitting.

The authors desire to express their indebtedness to their colleague Mr. G. E. Gardam for his valuable co-operation during part of this investigation.

**SUMMARY.**

A survey has been given of published information bearing upon the nature and occurrence of the defect known as "pitting" which occurs in electrodeposited metals.

Examples of pitting have been obtained in deposits of nickel, iron, cobalt, zinc and copper. Differences have been observed in the shape, internal lustre and distribution of the pits, and considerations of the probable causes of these differences have been discussed.

Observations of a magnified portion of the cathode surface during deposition have indicated that a pit is produced in a nickel deposit either by a bubble of gas clinging to the cathode surface for a prolonged period during deposition, or by a succession of bubbles proceeding from a particular point on the cathode surface.

When anodes and solutions of commercial purity were replaced by highly purified materials, it was found that pitting of the deposit was of less frequent occurrence and was localised above defects in the cathode surfaces where bubbles of gas formed and accumulated during deposition. This was particularly noticeable in cold rolled mild steel containing oxide inclusions and in brass sheet containing spills. Examination of a cross-section of some of the pits showed the presence of surface defects at their bases. In certain cases, by machining off a thin layer of metal from the cathode surface, the defects were removed and a pitless nickel deposit could then be formed.

A more generally applicable method consisted in first coating the surface of the cathode with copper. In the case of a steel cathode having surface defects a preliminary coating with nickel followed by a coating with copper deposited from the acid copper sulphate bath was found to prevent pitting of the final deposit of nickel. Similarly beneficial results could be obtained by coppering defective brass prior to nickel deposition.

The visual observation that a greater discharge of hydrogen occurs at a steel

surface compared with a similar surface coated with electrodeposited copper has been confirmed by cathode efficiency tests. The beneficial effect of the copper would appear to consist not only in covering up these defects and thereby eliminating these areas of lower overvoltage but also in providing a basis metal for nickel deposition upon which the overvoltage of hydrogen discharge is higher than upon steel. Determination of the solubility of hydrogen in nickel depositing solutions has indicated that a not inconsiderable amount of hydrogen may be evolved at the cathode surface during nickel deposition without appearing in the form of bubbles.

In nickel deposition with anodes and solutions of ordinary commercial purity, it has been found that pitting occurs not only as a result of defects in the basis metal but also as a consequence of a defective condition in the solution. Pitting of the former type may be conveniently referred to as "Basis Metal Pitting" and pitting of the latter type as "Solution Pitting." The possibility of eliminating basis metal pitting on a cathode by means of a preliminary deposit of copper of a suitable thickness renders it possible to ascertain whether a particular nickel plating solution is giving rise to solution pitting and is thus of great value in investigations upon the causes and methods for the prevention of pitting of the latter type.

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# THE HYDROLYSIS OF SOLUTIONS OF ZINC SULPHATE AND THE PRESENCE OF MONOVALENT ZINC IONS.

By H. G. DENHAM AND N. A. MARRIS.

*Received 23rd July, 1928.*

In 1908 it was definitely established by one of us<sup>1</sup> that measurements of the  $\rho_H$  value of solutions of zinc sulphate by means of a hydrogen electrode gave a variable value, the hydrolysis varying irregularly from day to day and failing to reach an equilibrium even after the expiration of four weeks. At the time the most plausible suggestion to put forward in an attempt to explain this periodic variation was that something in the nature of a pseudo-colloidal basic salt had separated out, hence the failure of the usual laws of hydrolysis to apply. Subsequent work with the closely allied element, cadmium, has shown that the hydrogen electrode is capable of effecting a reduction of the divalent cadmium ion to a monovalent state,<sup>2</sup> and the possibility of reduction of the closely related divalent zinc ion at the surface of the hydrogen electrode at once presents itself. Such reduction, coupled with a variable rate of diffusion of the acid produced in accordance with the equation



would naturally lead to an irregular  $\rho_H$  value as recorded by the hydrogen electrode. Information on this question was sought by replacing the hydrogen electrode by a quinhydrone half-element, which operates at a solution pressure of hydrogen  $10^{-24.4}$  of an atmosphere at 18° C., possibly too low a pressure to reduce in any way divalent zinc ions.

The quinhydrone used in these experiments was supplied by British Drug Houses, Ltd., and gave at 25° C. results strictly comparable with those published by O'Sullivan<sup>3</sup> for the cell

$\text{H}_2/\frac{N}{20}\text{Na}_2\text{SO}_4 + \frac{N}{200}\text{H}_2\text{SO}_4//$ same electrolyte // same electrolyte	+ quinhydrone/Pt.
Time.	E.M.F.
0 min.	.6987
15 mins.	.6990
30 mins.	.6990 <sup>4</sup>

The zinc sulphate used in the preliminary experiment was of A.R. quality, further purified by precipitation from a saturated solution by means of absolute alcohol and dried at 100° C. The zinc sulphate used in the main experiments was also of A.R. quality, precipitated from a saturated solution as above, the crystals redissolved to form a saturated solution at 70° C. and precipitated by cooling to the freezing-point. The hydrogen electrode was of platinum wire coated according to current practice with platinum black.

The platinum electrodes used in the quinhydrone half-elements were of

<sup>1</sup> *Z. anorg. Chem.*, 1908, 57, 378.

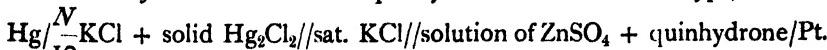
<sup>2</sup> Denham, *J. Chem. Soc.* (1908), 93, 834.

<sup>3</sup> *Trans. Far. Soc.*, 1925-26, 21, 319.

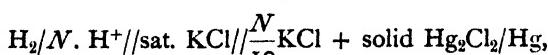
<sup>4</sup> Cf. Biilmann, *Ann. Chem.*, 1921 (IX.), 15, 109-157.

foil, 1 sq. cm. in area. Electromotive force measurements at 25° C. were made by means of a Leeds-Northrup potentiometer, a sensitive pointer galvanometer and a standard Weston cell. The results may be taken as correct to 0.0002 volt. All measurements were made against an  $N/10$  calomel electrode (0.6146 volt at 25° C.) The normality of all solutions is expressed in moles per litre.

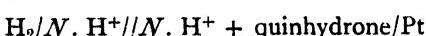
*Method of Calculation.*—The quinhydrone cell was of the type,



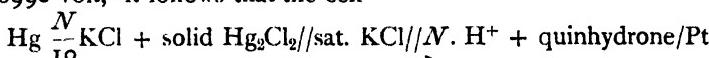
Since at 25° C. the *E.M.F.* of the cell,



is 0.3376 volt<sup>5</sup> and the *E.M.F.* of the cell



is 0.6990 volt,<sup>4</sup> it follows that the cell



is 0.3614 volt. If the *E.M.F.* of the cell



is  $\alpha$  volts, it follows that

$$0.3614 - \alpha = 0.0595 \log X$$

$$\text{whence } \log X = \frac{0.3614 - \alpha}{0.0595} = \rho_H$$

In actually carrying out the measurements it was found that with the hydrogen electrode from five to ten minutes were required to secure a steady value, whilst with the quinhydrone electrode a constant potential was instantly recorded.

Preliminary experiments were designed to test to what extent the variable  $\rho_H$  value previously noted in solutions of zinc sulphate was peculiar to the hydrogen electrode. The  $\rho_H$  given by solutions of zinc sulphate,  $N/16$ ,  $N/32$ , and  $N/64$  in strength was daily measured both with the hydrogen and the quinhydrone electrode over a period of a fortnight. The results given by  $N/32\text{ZnSO}_4$  are recorded in Table I., those given by the other solutions being entirely concordant.

The constancy of the results given by the quinhydrone electrode establishes the value of this electrode as a means of recording low hydrogen ion values arising from the hydrolysis of salt solutions, whilst, on the other hand, the marked change in acid concentration given by the hydrogen electrode indicates that some factor is here concerned which does not operate in the quinhydrone cell. The authors are of the opinion that a sufficient explanation of the above facts is afforded by the assumption that the hydrogen electrode is responsible for a reduction of zinc ions present in the surface layer of the electrode in accordance with the equation



<sup>5</sup> Clark, "Determination of Hydrogen Ions."

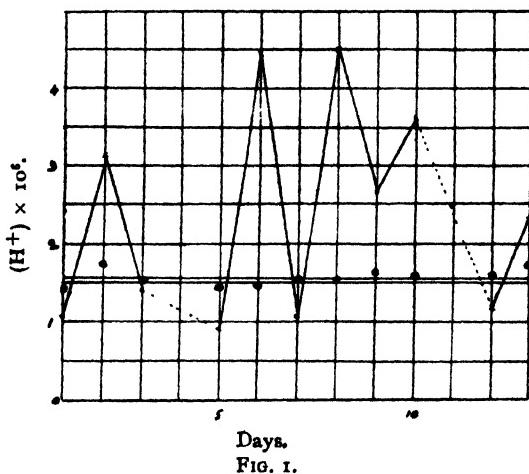
TABLE I.

*N/32 ZnSO<sub>4</sub>.*

Hydrogen Electrode. $H_2/ZnSO_4//\text{sat. KCl}/\text{calomel electrode.}$			Quinhydrone Electrode. $Pt/ZnSO_4 + \text{quinhydrone}/\text{sat. KCl}/\text{calomel electrode.}$		
Day.	E.M.F.	(H) $\times 10^6$ .	Day.	E.M.F.	(H) $\times 10^6$ .
1st	0.6904	1.07	1st	0.0161	1.42
2nd	0.6625	3.15	2nd	0.0208	1.73
3rd	0.6834	1.41	3rd	0.0178	1.52
5th	0.6939	0.94	5th	0.0151	1.41
6th	0.6539	4.46	6th	0.0154	1.46
7th	0.6899	1.09	7th	0.0182	1.57
8th	0.6539	4.46	8th	0.0177	1.53
9th	0.6671	2.66	9th	0.0191	1.62
10th	0.6591	3.64	10th	0.0188	1.60
12th	0.6880	1.18	12th	0.0188	1.60
13th	0.6705	2.34	13th	0.0206	1.72

These results are shown in Fig. I.

and that the actual value of the hydrogen ion concentration recorded by the electrode is conditioned by this reduction as well as by diffusion into the bulk solution of the acid so produced. Presumably the low hydrogen pressure peculiar to the quinhydrone electrode is incapable of setting up such reduction. Confirmation of these views is afforded by the results described in the next section.



### Reduction of Zinc Ions to a Lower State of Valence.

The potential given by the hydrogen electrode in solutions of zinc sulphate would, on

the above assumptions, be intimately linked with the manner in which the surface layer of the electrode was disturbed by the incoming hydrogen stream. An apparatus was constructed containing two such electrodes either of which could be connected through the middle vessel to the calomel. The first of the electrodes was saturated with hydrogen as usual from below, but in the second vessel the electrode was saturated by diffusion from the gaseous space above (Fig. 2). In order to test the apparatus both electrode cells were filled with *N/32 K<sub>2</sub>PO<sub>4</sub>*. Pure hydrogen was then led through both solutions for ten minutes, the electrode in II. being lifted right out of the liquid. This procedure was adopted in order to displace dissolved air from the solution. The stream of hydrogen was then discontinued, electrode II. lowered to the normal position, the stream of hydrogen started again but in such a way that electrode II. was

saturated from above. The *E.M.F.* of the phosphate solution against an *N/10* calomel electrode was then measured.

TABLE II.

Solution.	Time.	Electrode I.	Electrode II.
<i>N/32</i> KH <sub>2</sub> PO <sub>4</sub>	1 hr.	0·5735	0·5735
	2 hrs.	0·5745	0·5745
	3 hrs.	0·5745	0·5745
	6 hrs.	0·5745	0·5745
Equally satisfactory results were given by a solution of dilute sulphuric acid. The apparatus was then filled with <i>N/16</i> ZnSO <sub>4</sub> solution and the experiment repeated.			
<i>N/16</i> ZnSO <sub>4</sub>	50 mins.	0·6301	0·6403
	1 hr. 30 mins.	0·6483	0·6481
	2 hrs.	0·6475	0·6536
	3 hrs.	0·6565	0·6544
	4 hrs.	0·6589	0·6568
	5 hrs.	0·6600	0·6580
	6 hrs.	0·6592	0·6531
After standing overnight under a slight hydrogen pressure, the hydrogen stream was again started when the following readings were obtained:			
	23 hrs.	0·6576	0·6383
	23½ hrs.	0·6654	0·6441
	24 hrs.	0·6674	0·6421

A repetition of this experiment using a different sample of zinc sulphate showed an equally striking difference in the *pH* given by the two electrodes, indicating that reduction in the surface-layer was definitely taking place, the actual *pH* recorded being an equilibrium value determined not only by the rate of reduction but also by the rate of diffusion out of the surface layer.

An effort was then made to carry out far-reaching reduction of zinc sulphate by means of platinum black kept vigorously stirred in the solution of zinc sulphate by a vigorous stream of hydrogen. The platinum black was thoroughly washed with dilute ammonia, then repeatedly with distilled water, and finally with some of the reagent

with which it was subsequently to be used. In the first place an *N/32* KH<sub>2</sub>PO<sub>4</sub> solution was treated with platinum black prepared as above described, the hydrogen ion concentration as given by the quinhydrone electrode being  $9\cdot6 \times 10^{-5}$ . Hydrogen was then led vigorously through the solution for seven hours when the hydrogen ion concentration

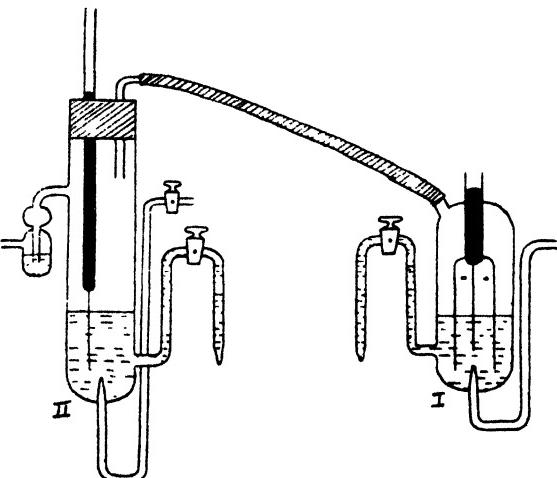


FIG. 2.

was found to be  $9.9 \times 10^{-5}$ . Similarly an  $N/32\text{KHSO}_4$  solution ( $[\text{H}^+] = 1.41 \times 10^{-2}$ ) gave after five hours' treatment with hydrogen a value  $1.34 \times 10^{-2}$ . No further change took place after a subsequent six hours' bubbling. The next step was to shake an approximately  $N/16\text{ZnSO}_4$  solution with platinum black for a few minutes and to record its hydrogen ion concentration by means of the quinhydrone electrode ( $2.27 \times 10^{-5}$ ). Hydrogen was then led through the solution and at intervals samples of the liquid were removed, filtered, and the hydrogen ion value determined as usual. After 10 hours' bubbling the cell

Pt/ $N/16\text{ZnSO}_4$  + quinhydrone//saturated KCl// $N/10$  calomel electrode gave:

Time.	E.M.F.	$(\text{H}) \times 10^5$
0 min.	0.1874	1.14
10 mins.	0.1874	1.14
15 mins.	0.1874	1.14
After 20 hours' treatment.		
0 min.	0.1911	1.32
20 mins.	0.1911	1.32
40 mins.	0.1911	1.32
After 24 hours.		
0 min.	0.1890	1.21
10 mins.	0.1890	1.21
20 mins.	0.1890	1.21

A second experiment gave strictly concordant results. An increase in the acid concentration to the extent of about 500 times had therefore been brought about by a reduction of the zinc ion. In view of the position of zinc in the electropotential series, the most plausible assumption to represent this reduction would be



### Hydrolysis of Zinc Sulphate.

Zinc sulphate (A.R. quality) was twice recrystallised, a stock solution made up, the strength of which was controlled by gravimetric analysis. All solutions gave a constant E.M.F. for at least half an hour.

TABLE III.

Dilution.	E.M.F.		Mean.	$(\text{H}) \times 10^5$	Per Cent. Hydrolysis
	A.	B.			
$v = 16$	0.0488	0.0498	0.0493	5.25	0.0042
$v = 32$	0.0478	0.0488	0.0483	5.05	0.0080
$v = 64$	0.0506	0.0602	0.0599	7.93	0.025
$v = 128$	0.0629	0.0632	0.0631	8.97	0.057
$v = 256$	0.0737	0.0722	0.0730	13.19	0.169

These results are lower than those hitherto recorded (H. Long, *J. Amer. Chem. Soc.*, **18** (1896), 693 gives 0·016 per cent. hydrolysis for an  $N/2\text{ZnSO}_4$  solution at  $20^\circ\text{C}$ .; H. Ley, *Z. physik. Chem.*, 1899, **30**, 193, gave 0·03 per cent. for  $N/16\text{ZnSO}_4$  at  $25^\circ\text{C}$ .; Carrara and Vespiagnani, *Gazz. Chim. Ital.*, 1900, **30**, ii, 35, records 0·0075 for  $N/2\text{ZnSO}_4$  at  $25^\circ$ .

### Summary.

(1) In contradistinction to the hydrogen electrode, the quinhydrone electrode has been found to give a perfectly steady value for the hydrolysis of zinc sulphate solutions.

(2) The apparent irregular variations in the hydrolysis of such solutions as recorded by the hydrogen electrode are attributed to the action of the hydrogen in reducing the zinc ion to a lower state of valence.

(3) The hydrolysis of solutions of zinc sulphate has been determined by means of the quinhydrone electrode.

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## THE HYDROLYSIS OF CERTAIN EASILY REDUCIBLE METALLIC SALTS.

By H. G. DENHAM AND N. A. MARRIS.

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The suitability of the quinhydrone electrode for the determination of the hydrolysis of zinc sulphate which undergoes reduction at the surface of the hydrogen electrode has been demonstrated by the authors in the preceding paper. The work has been extended to certain salts which have previously been shown to be capable of similar reduction.<sup>1</sup> In all cases referred to in this paper, the procedure of measurement, etc., was strictly in accordance with that laid down in the preceding paper.

### Cadmium Sulphate.

A series of measurements of the cell (A),  $\text{H}_2$  in  $\text{Pt}/N/16\text{CdSO}_4//$  saturated  $\text{KCl}/N/10$  calomel electrode, and of the cell (B),  $\text{Pt}/N/16\text{CdSO}_4+$  quinhydrone//saturated  $\text{KCl}/N/10$  calomel electrode, was made in order to test and compare the relative reducing power of the two electrodes.

The steady change in the measured *E.M.F.* of Cell A clearly demonstrates the unsuitability of the hydrogen electrode as a means of measuring the hydrolysis of cadmium sulphate, whilst it is equally clear that the quinhydrone electrode gives remarkably steady values for such work. Table II. records the mean values for the hydrolysis of a series of solutions of cadmium sulphate (A.R. quality) as given by two different quinhydrone electrodes.

<sup>1</sup> Denham and Allmand, *J. Chem. Soc.*, 1908, **93**, 424; Denham, *J. Chem. Soc.*, 1908, **93**, 833.

TABLE I.

Time.	E.M.F. Cell A.	Time.	E.M.F. Cell B.
0	0.1748	0	{ a 0.0124 b 0.0124
29 mins.	0.2998	24 mins.	{ a 0.0123 b 0.0123
46 "	0.3415	1 hr.	{ a 0.0124 b 0.0124
1 hr.	0.3657	2½ hrs.	{ a 0.0123 b 0.0125
3½ hrs.	0.4052	3½ "	{ a 0.0125 b 0.0125
6½ "	0.4324	6 "	{ a 0.0125 b 0.0125
10 "	0.4478		

TABLE II.

Dilution.	E.M.F.	(H <sup>+</sup> ) × 10 <sup>6</sup> .	Per Cent. Hydrolysis.
v = 16	0.0124	1.54	.012
v = 32	0.0656	0.99	.016
v = 64	0.0575	0.72	.023
v = 128	0.0560	0.68	.044
v = 256	0.0486	0.51	.065

These results show reasonable agreement with those of Carrara and Vespiagnani,<sup>2</sup> who found 0.017 per cent. hydrolysis for an N/10 solution of cadmium sulphate at 25° C. It may be mentioned that O'Sullivan<sup>3</sup> failed to obtain a constant E.M.F. for the cell

$H_2/N/20CdSO_4 + N/200H_2SO_4$ /same electrolyte + quinhydrone/Pt, the E.M.F. showing a steady increase with time, an effect which the author attributed to a poisoning of the hydrogen electrode. A more probable explanation is afforded by the results shown in Table I. above, wherein the marked reducing action of the hydrogen electrode upon aqueous solutions of cadmium sulphate is made tolerably certain.<sup>1</sup> It is therefore suggested that the trend in O'Sullivan's E.M.F. for the above cell has its origin in a progressive reduction at the surface of the hydrogen electrode, symbolised in the equation  $Cd^{++} + H \rightarrow Cd^+ + H^+$ .

### Lead Chloride.

Allmand and Denham<sup>1</sup> have shown that the hydrogen electrode is unsuitable for measuring the  $\rho_H$  value of an aqueous solution of lead salts in as much as progressive reduction of the divalent lead ion to a monovalent state takes place, whilst one of the authors has shown that a series of sub-valent lead salts may be prepared from lead suboxide.<sup>4</sup> It was hoped that this difficulty of reduction would not be experienced when the hydrogen electrode was replaced by the quinhydrone half-element.

The sample of lead chloride was prepared from Merck's pure lead

<sup>1</sup> Gazz. Chim. Ital., 30, ii., 35, 1900.

<sup>2</sup> Trans. Farad. Soc., 21, 1925-26, 321.

<sup>3</sup> Denham, J. Chem. Soc., 1917, 111, 244; 1918, 113, 249.

nitrate by precipitation with A.R. ammonium chloride. The precipitate was washed till free from ammonia, and then recrystallised. After filtration the sample was made into a stock solution  $N/50$  in strength, from which other solutions were prepared by dilution.

Readings of the cell  $\text{Pt}/N/50\text{PbCl}_2 + \text{quinhydrone}/\text{saturated ammonium nitrate}/\text{calomel electrode}$  were taken over an extended period and perfectly steady values recorded for each electrode.

TABLE III.—LEAD CHLORIDE.

$N/50\text{. PbCl}_2$		Dilution.	E.M.F.	$H \times 10^6$	Per Cent. Hydrolysis.
Time.	E.M.F.				
0	{ 0·1155 0·1150 }	v = 50	0·1152	6·85	0·17
		v = 100	0·1029	4·41	0·22
10	{ 0·1155 0·1155 }	v = 200	0·0925	2·82	0·28
		v = 400	0·0847	2·09	0·42
20	{ 0·1155 0·1150 }	v = 800	0·0810	1·80	0·72
40	{ 0·1155 0·1150 }				

### Lead Nitrate.

Merck's lead nitrate was used in these experiments. A preliminary test showed that the quinhydrone electrode gave a perfectly steady value over an extended period.

TABLE IV.—LEAD NITRATE.

Dilution.	E.M.F.	$H \times 10^6$ .	Per Cent. Hydrolysis.
v = 16	{ 0·1208 0·1214 }	8·60	0·069
v = 32	{ 0·1085 0·1080 }	5·21	0·084
v = 64	{ 0·0954 0·0954 }	3·16	0·102
v = 128	{ 0·0829 0·0833 }	1·96	0·136
v = 256	{ 0·0743 0·0737 }	1·37	0·175

The constancy of the potential of the quinhydrone electrode affords convincing evidence that in this case the hydrogen pressure is unable to bring about measurable reduction of the divalent lead ion.

### Thallous Sulphate.

Evidence has been adduced by one of the authors<sup>1</sup> which demonstrates the tendency of the thallous ion to be reduced to a subvalent state by metallic thallium, and it is therefore questionable whether the measurements of the hydrolysis of this salt, as recorded by the hydrogen electrode are entirely free from error arising from such reduction as has been indicated in the case of lead salts. Measurements have therefore been repeated with the quinhydrone electrode.

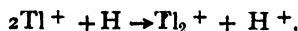
## 518 EFFECT OF ONE SALT ON SOLUBILITY OF ANOTHER

This salt was prepared from pure thallium by solution in dilute sulphuric acid. After filtration the sulphate was thrown down with absolute alcohol and well washed with alcohol. The crystals were re-dissolved in boiling water and the sulphate again precipitated with alcohol. After thorough washing the crystals were dried at  $120^{\circ}\text{C}$ . for one hour, and finally heated in an electric furnace to  $500^{\circ}\text{C}$ . The *E.M.F.* of the various cells remained perfectly constant for at least an hour.

TABLE V.—THALLOUS SULPHATE.

Dilution.	<i>E.M.F.</i>	$H \times 10^5$ .	Per Cent. Hydrolysis.
$v = 25$	{ 0·0613 0·0613}	0·84	0·010
$v = 50$	{ 0·0689 0·0680}	1·10	0·028
$v = 100$	{ 0·0705 0·0715}	1·22	0·061
$v = 200$	{ 0·0578 0·0578}	0·72	0·073
$v = 400$	0·0630	0·85	0·17
$v = 800$	0·0615	0·84	0·34

These values are distinctly lower than that recorded by Denham, using a hydrogen electrode, *viz.*, 4·9 per cent. for a  $N/16$   $\text{Tl}_2\text{SO}_4$  solution at  $25^{\circ}\text{C}$ . and it is suggested that in the latter case the measurements have been vitiated by reduction of the thallous ion to a subvalent state, *e.g.*



### Summary.

(1) The quinhydrone electrode has been used for the determination of the hydrolysis of solutions of cadmium sulphate, lead chloride, and nitrate and thallous sulphate.

(2) In all cases the electrode proved eminently suitable for the determination of the  $p_{\text{H}}$  values of these salts, previously shown to be easily reducible by the hydrogen electrode.

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## THE EFFECT OF ONE SALT ON THE SOLUBILITY OF ANOTHER IN ETHYL ALCOHOL SOLUTION, PART III.

By F. S. HAWKINS and J. R. PARTINGTON.

*Received 20th July, 1928.*

The relations existing between two comparatively soluble salts having an ion in common were described in Parts I. and II. of this series.<sup>1</sup> The calculation of the specific conductivities of the sodium iodide and thio-

<sup>1</sup> *Trans. Faraday Soc.*, 1927, 23, 522.

cyanate solutions by Barmwater's method, on p. 534, has been repeated, and the results are shown in Table I., which replaces Table VI. The calculated specific conductivities of the mixtures ( $K_1 + K_2$ ) given in the previous communication, remain practically unchanged.

TABLE I.

Expt.	Equiv. Concent.		$\frac{100}{\text{NaI}}$	$\frac{100}{\text{NaCNS}}$	$K_1$ $\text{NaI}$	$K_2$ $\text{NaCNS}$	$(K_1 + K_2)$
	NaI.	NaCNS.					
1	21.38	21.38	18.36	16.74	1.977	0.097	2.074
2	22.42	22.42	18.08	16.50	1.812	0.317	2.129
3	23.37	23.37	17.76	16.28	1.658	0.514	2.172
4	23.55	23.55	17.73	16.25	1.635	0.547	2.182
5	23.76	23.76	17.67	16.20	1.592	0.599	2.191

In Table VII., p. 534, experiment 3, the value of  $K_1$  should be 1.679.

In the present communication, the influence of sodium and magnesium iodides, both readily soluble, on the solubility of the moderately soluble potassium iodide in alcohol at 25° C. is recorded.

### Preparation of Materials.

*Ethyl Alcohol.*—This was prepared and stored according to the method given by King and Partington,<sup>2</sup> with the exception that any aldehyde present was removed by resinification with caustic soda. Removal of the aldehyde by means of silver nitrate may result in the formation of ethyl acetate, which is more difficult to remove than acetaldehyde. The density, corrected for buoyancy was  $D_4^{25} = 0.7851$ .

*Sodium Iodide.*—This salt was prepared by the process given by King and Partington<sup>2</sup> and dehydrated by heating *in vacuo*.<sup>3</sup> On precipitation with silver nitrate, the theoretical iodide content was found.

*Potassium Iodide.*—This was prepared by the above process, and also by recrystallising Kahlbaum's pure product from water and rejecting head or tail fractions. Traces of water were removed by powdering the salt, and heating it *in vacuo*. (Iodine found 76.46 per cent., theoretical 76.47 per cent.)

*Magnesium Iodide.*—This salt was obtained as the alcoholate by the method given by Menschutkin.<sup>4</sup> The crude product was recrystallised twice from dry alcohol in an atmosphere of oxygen-free hydrogen. (Iodide found 45.73 per cent., theoretical 45.77 per cent.)

### Solubility Determinations.

The solutions were made up in the flask shown (Fig. 1). The ground joint D was made to fit corresponding joints on the evaporating bottles, pipettes, pyknometer, and alcohol container used. The tap B served for the introduction of dry oxygen-free hydrogen. A convenient quantity of sodium iodide, or magnesium iodide, and sufficient potassium iodide to saturate the solution were roughly weighed out in a stoppered bottle and tipped into the flask. The ground stopper C was cemented in its place to

<sup>2</sup> *J. Chem. Soc.*, 1926, 128, 20.

<sup>3</sup> *Ibid.*, 1913, 29, 233.

<sup>4</sup> *Z. anorg. Chem.*, 1907, 52, 15.

prevent its being shaken out, and the air was displaced by hydrogen. The requisite quantity of alcohol was run in, and the last traces of air removed by again passing a current of hydrogen. The whole apparatus was shaken in an air thermostat at  $25^{\circ} \pm .05^{\circ}$  until equilibrium was reached, and then left for 12 hours in a water thermostat at  $25^{\circ} \pm .015^{\circ}$ . Trial analyses showed that, in all cases, equilibrium was reached after 24 hours' shaking.

In the case of sodium and potassium iodides, the solubilities of the mixed salts were determined by direct evaporation of the solution to dryness. One tube of the stopper of the evaporating bottle described by King and Partington<sup>2</sup> was ground to fit the joint D of the solubility flask. The bottle was weighed before and after filling, and also after the solution had been evaporated to dryness on the water bath in a current of hydrogen.

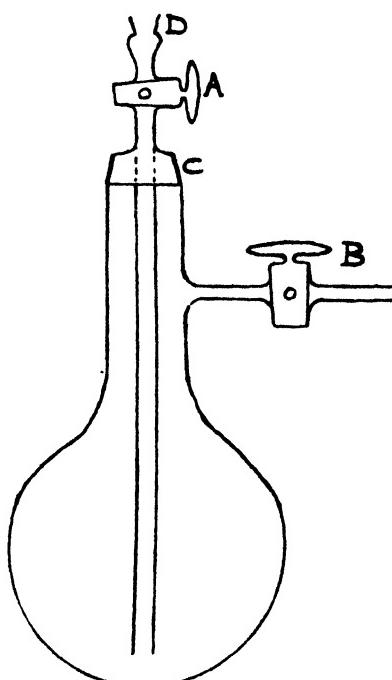


FIG. 1.—Solubility flask.

The potassium content of the solid was determined by the method previously published.<sup>5</sup>

The solubilities of mixtures of magnesium and potassium iodides could not be determined by evaporation as magnesium iodide separates out as the alcoholate, so in this case a known weight of solution was weighed in a pipette fitted with ground-on caps, diluted with water and its iodide content determined by precipitation with silver nitrate. Preliminary experiments showed that the solubility of silver iodide in aqueous alcohol was negligible. As magnesium perchlorate<sup>6</sup> is easily soluble in alcohol, the potassium content was obtained by the same method as before, the amount of alcohol retained by the magnesium iodide being too small to dissolve appreciable quantities of potassium perchlorate. It was found that determinations of the magnesium content by Gibbs' method gave results that were too high when the analysis was carried out in aqueous alcohol.

By evaporating to dryness, taking up the residue in water, evaporating, and repeating this process, the alcohol of crystallisation was removed and the magnesium content could be obtained. The precipitate of magnesium ammonium phosphate obtained after this process, however, blackened extremely readily in the subsequent ignition, and useful results were only obtained by very careful heating. It was felt that more confidence could be placed in the potassium determinations, and these were used to obtain the final values.

To convert the solubilities, expressed as gms./100 gms. solvent to gms./c.c. the densities were obtained by fitting a V-shaped pyknometer into the joint D of the solubility flask, filling it by passing hydrogen through tap

<sup>5</sup> *J. Chem. Soc.*, 1927, 1397.

<sup>6</sup> Willard and Smith, *J. Amer. Chem. Soc.*, 1923, 45, 293.

B, setting it when in the thermostat at  $25^{\circ}$ , and weighing it after it had been dried and left to attain the temperature of the balance case.

The solubilities and densities obtained are given below:—

TABLE II.  
POTASSIUM IODIDE IN THE PRESENCE OF SODIUM IODIDE.

Conc. of NaI.		Conc. of KI.		$D_{45}^{25}$ .
Gms./100 g. EtOH.	Moles/c.c. $\times 10^5$	Gms./100 g. EtOH.	Moles/c.c. $\times 10^5$	
—	—	1.824	8.606	.7970
4.248	22.05	1.268	5.947	.8215
7.091	36.65	1.9988	4.662	.8378
9.065	46.74	1.8878	4.735	.8502
15.84	88.9	1.6752	3.114	.8921
27.68	138.56	1.442	1.905	.9014
42.8	209.6	1.19	0.8406	1.0500

A previous determination of the solubility of potassium iodide has been made by Walden,<sup>7</sup> who obtained a mean value of 1.922 gms./100 gms. alcohol at  $25^{\circ}$ . The value 1.824 gms./100 gms. alcohol was obtained as the mean of four experiments, made after the solution had been in the thermostat for a week. The separate values were:—

1.812	gms./100 gms. EtOH
1.832	" "
1.835	" "
1.818	" "
Mean 1.824	" "

The alcohol used was probably drier than that used by Walden.

TABLE III.  
POTASSIUM IODIDE IN THE PRESENCE OF MAGNESIUM IODIDE.

Conc. of MgI <sub>2</sub>		Conc. of KI.		$D_{45}^{25}$ .
Gms./100 g. EtOH.	Moles/c.c. $\times 10^5$	Gms./100 g. EtOH.	Moles/c.c. $\times 10^5$	
—	—	1.824	8.606	.7970
2.777	7.8	1.502	7.085	.8161
3.20	9.015	1.513	7.14	.8202
5.53	15.54	1.578	7.43	.8317
6.017	16.92	1.56	7.349	.8420
8.809	24.85	1.393	6.558	.8634
14.41	40.64	1.195	5.627	.9037
17.82	48.54	1.116	5.205	.9182
18.04	51.17	—	—	.9314

The solubility of magnesium iodide as determined by Menschutkin<sup>4</sup> is 18.1 gms./100 gms. EtOH at  $25^{\circ}$  which is in good agreement with the value found above.

<sup>7</sup> Z. physik. Chem., 1906, 55, 715.

### Theoretical Treatment.

When the solubilities of potassium iodide are plotted as ordinates against the concentration of sodium or magnesium iodide (Fig. 2), the curve shows a steady decrease in the solubility of potassium iodide in the presence of increasing quantities of sodium iodide, but in the case of the other salt pair the solubility of potassium iodide passes through a minimum and maximum as the concentration of magnesium iodide increases.

The compound  $MgI_2 \cdot KI \cdot 6H_2O$ , analogous to carnallite has been described by Lerch,<sup>8</sup> and de Schulten,<sup>9</sup> and the inflexions on the curve can be explained by assuming an equilibrium between the complex  $MgI_2 \cdot KI$ , and its constituent ions in solution, although the compound  $MgI_2 \cdot KI \cdot x EtOH$  does not seem to have been described. The solubilities are expressed in mols./c.c. and in subsequent calculations this unit will be used.

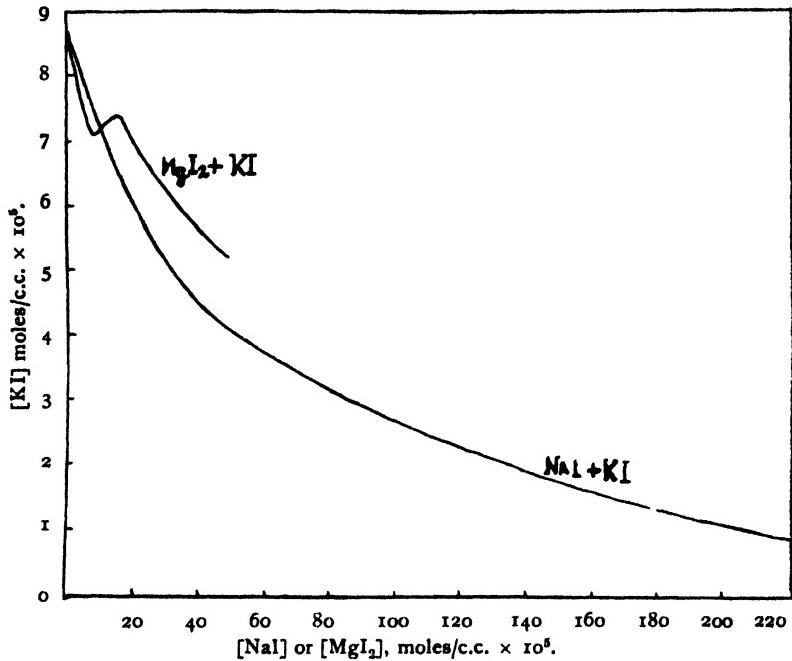


FIG. 2.

Partington and King<sup>1</sup> found that the solubility of sodium iodide in solutions containing sodium thiocyanate was represented by the equation

$$S = S_0 e^{-Bc}$$

where

$S_0$  = Solubility of sodium iodide in alcohol.

$S$  = " " " " " a solution containing sodium thiocyanate of concentration  $c$ .

This equation has been found empirically to represent the change of solubility of a non-electrolyte when dissolved in an electrolyte of concentration  $c$ , and can be applied by plotting  $\log S/S_0$  against  $c$ . In the case under discussion the plot is not linear over any range of concentration (Fig. 3).

<sup>8</sup> J. Pr. (2), 28, 338.

<sup>9</sup> Bull. Soc. Chem., 1900 (3), 33, 158.

TABLE IV.  
SODIUM AND POTASSIUM IODIDES. MAGNESIUM AND POTASSIUM IODIDES.

$-\log \frac{S}{S_0}$	[NaI] $\times 10^5$ .	$-\log \frac{S}{S_0}$	[MgI <sub>2</sub> ] $\times 10^5$ .
0.1605	22.05	0.0845	7.8
0.2662	36.05	0.0811	9.015
0.3183	46.74	0.0638	15.54
0.4414	80.9	0.0686	16.92
0.6549	138.56	0.1181	24.85
1.0102	209.6	0.1846	40.64
—	—	0.2184	48.54

A. A. Noyes<sup>10</sup> has applied the theory propounded by Debye and Hückel to the mutual solubilities of salts, and for a uni-univalent salt obtains the expression

$$-\frac{1}{2} \ln \frac{f_A f_B}{f_{A_0} f_{B_0}} = \frac{A}{R(KT)^3} (\sqrt{2\mu} - \sqrt{2\mu_0})$$

where

$$A = e^2 \bar{n}^2 \sqrt{\pi/R}.$$

[MgI<sub>2</sub>] or [NaI] in moles/c.c.  $\times 10^5$ .

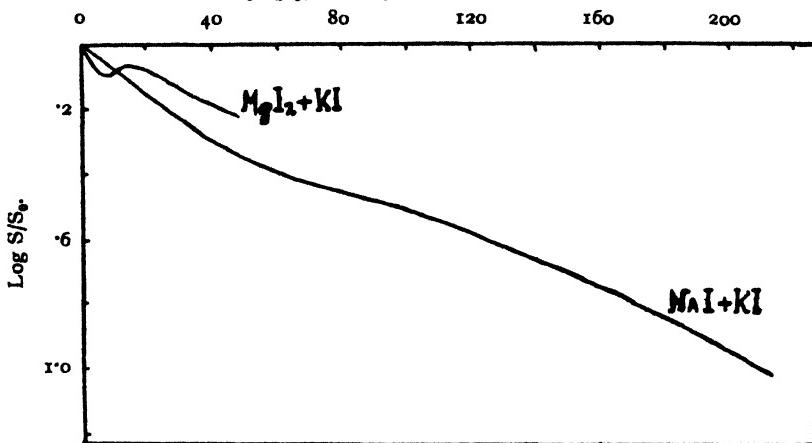


FIG. 3.

$f_{A_0}, f_{B_0}$  = Activity coefficients of the ions A and B when dissolved in a pure solvent.

$f_A, f_B$  = Their activity coefficients when dissolved in a solution of another salt.

$k$  = Dielectric constant.

$\mu_0$  = Ionic strength of the salt AB dissolved in the pure solvent.

$\mu$  = Ionic strength of a solution of the two salts.

$\bar{n}$  = Number of molecules/mole.

$e$  = Electronic charge.

In the case of two salts with a common ion,

$$c_A f_A \cdot c_B f_B = c_{A_0} f_{A_0} \cdot c_{B_0} f_{B_0}$$

where  $c_A, c_B$  etc. are the ionic concentrations corresponding to  $f_A, f_B$  etc.

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Substituting the numerical values for the constants, and converting to common logarithms gives

$$-\frac{1}{2} \log \frac{c_{A_0} c_{B_0}}{c_A c_B} = 58.97 (\sqrt{2\mu} - \sqrt{2\mu_0}) \text{ at } 25^\circ \text{ C.}$$

The value of the dielectric constant used is that given by Nernst, i.e., 26 C.G.S. units at  $25^\circ$ .

The ratio of the products  $c_{A_0} c_{B_0}/c_A c_B$  is called the activity product ratio by Noyes, and its logarithm denoted by  $\log A.P.R.$ . This notation will be used in the paper, and the data for the two salt pairs are given in Table V.

TABLE V.—SODIUM AND POTASSIUM IODIDES.

$[NaI] \times 10^5$	$[KI] \times 10^5$	$-\frac{1}{2} \log A.P.R.$	$\sqrt{2\mu}$
—	8.606	—	.01312
22.05	5.947	.1759	.02366
36.65	4.662	.2076	.02874
46.74	4.135	.2267	.03189
80.90	3.114	.2741	.04097
138.56	1.905	.2788	.05299
209.6	0.8406	.1819	.06486

TABLE VI.—MAGNESIUM AND POTASSIUM IODIDES.

$[MgI_2] \times 10^5$	$[KI] \times 10^5$	$-\frac{1}{2} \log A.P.R.$	$\sqrt{2\mu}$
—	8.606	—	.01312
7.80	7.085	.1682	.02469
9.015	7.140	.1925	.02616
15.54	7.430	.2935	.03288
16.92	7.349	.3056	.03409
24.85	6.588	.3497	.04028
40.64	5.627	.4098	.05050
48.54	5.200	.4282	.05491

The plot of these figures shows that the relation does not hold at the concentrations measured (Fig. 4). The shape of the curve for sodium and potassium iodides suggests, however, that at low concentrations, the relation will hold, and this agrees with the work of Brönsted<sup>11</sup> with aqueous solutions, but differs from the conclusions drawn by Kraus and Seward,<sup>12</sup> who used solutions in acetone and isopropyl alcohol. Robinson,<sup>13</sup> however, who also used acetone, concludes that the change in solubility is of the order of magnitude to be expected from the theory of Debye and Hückel. He had difficulty in obtaining consistent analyses, but the relation between  $\frac{1}{2} \log A.P.R.$  and  $\sqrt{2\mu}$ , as shown in his diagram, really gives an individual curve for each salt pair, and this is in agreement with Kraus and Seward.

The curve for solutions of potassium iodide in magnesium iodide and alcohol possesses some unexpected features. At the lowest concentrations measured, the graph is a straight line, as required by the theory of complete

<sup>11</sup> *J. Amer. Chem. Soc.*, 1926, **48**, 2015.

<sup>12</sup> *Trans. Faraday Soc.*, 1927, **23**, 488.

<sup>13</sup> *J. Physical Chem.*, 1928, **32**, 1089.

dissociation, but it is at these concentrations that the plot of the solubilities (Fig. 2) shows a maximum and minimum, and this was ascribed to the formation of a complex  $MgI_2 \cdot KI$  in solution. It is difficult to reconcile these two facts, but it is possible that the increase in solubility due to the formation of the complex is just sufficient to balance the decrease due to the salting-out effect of the ions, and the agreement with the Debye theory is then accidental.

To account for the mutual salting-out effect of the ions in more concentrated solutions, Brönsted<sup>14</sup> proposed the equation

$$-\frac{1}{2} \log A.P.R. = 3\alpha(\sqrt{2\mu} - \sqrt{2\mu_0}) + \beta c$$

where  $c$  = Concentration of added salt and  $\alpha$  and  $\beta$  are constants.

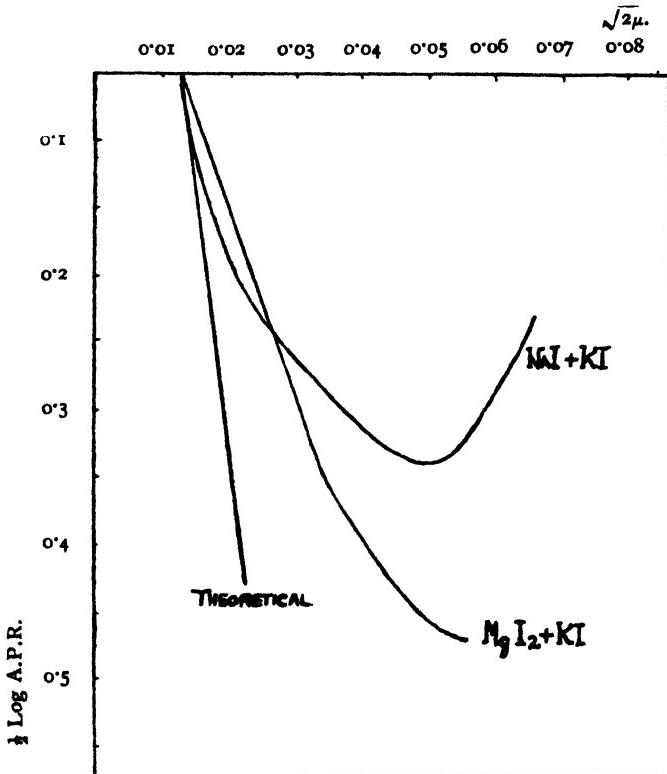


FIG. 4.

This may conveniently be applied by solving for  $\alpha$  and  $\beta$  at the two lowest concentrations, and then calculating  $\beta$  at other concentrations from the value of  $\alpha$  obtained. A constant value for  $\beta$  will be obtained over the range where the equation holds.

Table VII shows that the equation holds for this salt pair for concentrations up to  $0.5N$ . The constant  $3\alpha$  is smaller than the corresponding figure calculated from the universal constants on the theory of Debye and Hückel. In the latter case, however, the value of the dielectric constant used is that of the solvent in bulk, whereas the theory requires that the

<sup>14</sup> *J. Amer. Chem. Soc.*, 1921, 43, 2265.

TABLE VII.—SODIUM AND POTASSIUM IODIDES.

$[NaI] \times 10^5$ .	$-\frac{1}{2} \log A.P.R.$	3a.	$-\beta \times 10^{-5}$ .
22.05	1759	44.44	+ 0.01327
36.65	2076	"	- 0.01327
46.74	2276	"	- 0.01336
80.9	2741	"	- 0.01193
138.56	2788	"	- 0.01078
209.6	1819	"	- 0.01007

dielectric constant of the solution in the neighbourhood of the ions should be used.

If Brönsted's equation is applied to the solutions of magnesium and potassium iodides over the range where the plot of  $-\frac{1}{2} \log A.P.R.$  against  $\sqrt{2\mu}$  is a curve the results in Table VIII. are obtained.

TABLE VIII.—MAGNESIUM AND POTASSIUM IODIDES.

$[MgI_2] \times 10^5$ .	$-\frac{1}{2} \log A.P.R.$	3a.	$-\beta \times 10^{-5}$ .
16.92	3056	27.4	- 0.01588
24.85	3497	"	- 0.01588
40.64	4098	"	- 0.01511
48.54	4282	"	- 0.01477

The agreement between the values of  $\beta$  is not good.

The expression for the activity coefficient of an ion used by Noyes is derived on the assumption that the ion can be regarded as a point charge, and this is only tenable in dilute solutions. Scherer<sup>15</sup> has derived the following expression for the activity coefficient of an ion of radius  $a$ ,

$$-\ln f = \frac{\sqrt{\pi n} \left( \frac{e}{KkT} \right)^{3/2} v^2 \sqrt{2\mu}}{1 + a \sqrt{\frac{4\pi e^2 n}{KkT}} \sqrt{2\mu}}.$$

$k$  = Boltzmann's constant

$v$  = Valency of an ion.

For a uni-univalent salt this can be substituted in the expression,

$$c_{A_0} f_{A_0} \cdot c_{B_0} f_{B_0} = c_A f_A \cdot c_B f_B$$

and on evaluating the constants, the expression for  $\log A.P.R.$  becomes

$$-\frac{1}{2} \log A.P.R. = \frac{58.97 \sqrt{2\mu}}{1 + 1.278 \times 10^6 a \sqrt{2\mu}} - \frac{58.97 \sqrt{2\mu_0}}{1 + 1.278 \times 10^6 a \sqrt{2\mu_0}}.$$

If each of the terms on the right-hand side of this equation is written in the form  $b \sqrt{x}(1 + ac \sqrt{x})^{-1}$  and expanded for two terms, the equation

$-\frac{1}{2} \log A.P.R. = 58.97(\sqrt{2\mu} - \sqrt{2\mu_0}) - 58.97 \times 1.278 \times 10^6 a (2\mu - 2\mu_0)$  is obtained, and this is in the same form as Brönsted's salting-out equation, but  $(2\mu - 2\mu_0)$  is not equal to  $c$ , but to  $c + s - s_0$  where

$c$  = Conc. of added salt.

$s$  = Conc. of a saturated solution of a salt in the salt solution of concentration  $c$ .

$s_0$  = Conc. of a saturated solution of a salt in the pure solvent.

The equation in its unexpanded form can be solved as a quadratio in  $a$ , and the positive root is given in Table IX.

TABLE IX.  
SODIUM AND POTASSIUM IODIDES.

$-\frac{1}{2} \log A.P.R.$	$\sqrt{2\mu}$	$a \times 10^{-8}$
'1759	'02366	3'819
'2076	'02874	4'304
'2267	'03189	4'421
'2741	'04099	4'569
'2788	'05299	5'183
'1819	'06486	7'656

MAGNESIUM AND POTASSIUM IODIDES.		
'1682	'02469	4'304
'1925	'02616	4'099
'2935	'03288	3'544
'3056	'03409	3'538
'3497	'04028	3'601
'4098	'05050	3'634
'4282	'05491	3'670

The values of  $a$  obtained are of the correct order of magnitude, but they do not remain constant. No correction has been made for the change of dielectric constant with concentration, as the assumption made by Hückel<sup>16</sup> that the dielectric constant is a linear function of the concentration has not been justified by the experimental work of Walden, Ulich, and Werner,<sup>17</sup> and it was thought better not to apply a correction until the relation between these two quantities is really known. The absence of this correction must cause an error in the value of  $a$ , particularly in concentrated solutions, and measurements of the dielectric constant will be undertaken in order to determine its magnitude. It is noticeable that in the case of magnesium and potassium iodides the value of  $a$  passes through a minimum at the concentrations where the solubility is a maximum.

#### Viscosities and Conductivities.

The viscosities and conductivities of the above solutions were measured in a cell similar to that described in Part I. The viscosimeter tube, however, was placed in the stopper of the cell, and dipped into the liquid in the manner described by Scarpa.<sup>18</sup> This arrangement ensures that the liquid in the viscosimeter tube flows in the opposite direction to that in the body of the cell, and it was hoped by this means to eliminate the error caused by turbulence. The viscosities so obtained, however, were not in agreement with those obtained from the density of the solution and the time of fall by Ostwald's method. Ingham<sup>18a</sup> has also found discrepancies at negative pressures corresponding to those used in this work, but finds the method more accurate at lower pressures. Conductivities were measured in

<sup>16</sup> *Physik Z.*, 1925, 26, 93.

<sup>18</sup> *Gazz.*, 1910, 40, ii, 261.

<sup>17</sup> *Z. physik. Chem.*, 1925, 116, 261.

<sup>18a</sup> *J. Chem. Soc.*, 1928.

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the manner described in Part I., polarisation errors being kept at a minimum by reducing the cell current as much as possible, and amplifying the bridge current by a single valve amplifier. The conductivities and viscosities are given in Tables X. and XI.

TABLE X.—SODIUM AND POTASSIUM IODIDES.

[NaI] × 10 <sup>5</sup> .	Specific Conductivity.	Viscosity.	
		Scarpa.	Ostwald.
(KI alone)	.001429	.01105	.01114
22.05	.003548	.01253	.01229
36.65	.004957	.01323	.01335
46.74	.00575	.01415	.01355
80.9	.00828	.01689	.01670
138.56	.01607	.02261	.01851
209.6	.01941	.02858	.02758

TABLE XI.—MAGNESIUM AND POTASSIUM IODIDES.

[MgI <sub>2</sub> ] × 10 <sup>5</sup> .	Specific Conductivity.	Viscosity.	
		Scarpa.	Ostwald.
(KI alone)	.001429	.01105	.01114
7.8	.002442	.01198	.01158
9.015	.002767	.01239	.01187
15.54	.003134	.01365	.01545
16.92	.003233	.01418	.01414
24.85	.003886	.01660	.01599
40.64	.005022	.02118	.02027

and the results are given in Tables XII. and XIII.

TABLE XII.—MAGNESIUM IODIDE.

[MgI <sub>2</sub> ] × 10 <sup>5</sup> .	$\sqrt{[MgI_2]} \times 10^2$ .	Δ.
51.17	2.262	10.63
10.234	1.012	16.43
2.047	0.4523	24.35
0.4094	0.2022	37.25
0.0819	0.09045	51.71
0.01638	0.04045	62.18

Conductivity of Alcohol  $5.926 \times 10^{-6}$  reciprocal ohms.

TABLE XIII.—POTASSIUM IODIDE.

[KI] × 10 <sup>5</sup> .	Δ.	Δ <sub>0</sub> .
8.606	16.6	52.28
1.79	30.83	52.46
0.512	37.58	52.1
0.1809	42.02	52.27
0.09047	43.89	52.46
0.0716	44.44	52.2
0.01809	47.36	52.38
		Mean 52.31

The molecular conductivity of the magnesium iodide was plotted against the square root of its concentration (Fig. 5), giving the curve shown, which indicates that this electrolyte does not even approximately agree with the Debye-Hückel theory, in which case a straight line would have been found. It was also noted that the data could not be fitted to the equation  $\Lambda_0 = \Lambda + Bc^n$  by the method given by Ferguson and Vogel,<sup>19</sup> and that the Storch equation could only be applied over a small range of concentration without change of constants.

A number of workers have measured the conductivity of potassium iodide in alcohol at 25°. Walden<sup>20</sup> found that, after correcting for the conductivity of the solvent, it was given by the equation

$$\Lambda_0 = \Lambda + ac^{1/3}.$$

He used no solutions more concentrated than  $V = 64$  litres/mol. Turner,<sup>21</sup> who started with a 0.1*N* solution, which was diluted, did not find that the above relation held, but as a saturated solution at 25° is only 0.08606*N*, there seems to be some error in his work. Dutoit and Rappeport<sup>22</sup> obtained a value of  $\Lambda_0 = 45$ . As this has been exceeded by Walden at a dilution of  $V = 2048$  litres, one or both of these two sets of results must be incorrect. Philip and Courtman<sup>23</sup> obtained values which agreed fairly closely with Walden's figures.

Owing to this conflict of evidence the dissociation of potassium iodide was measured, and the results are given in Table XIII. It was found that they could be represented by the equation

$$\Lambda_0 = \Lambda + 699.1 c^{-3.18}$$

giving a mean value of  $\Lambda_0 = 52.31$ . The exponent of this equation is very near the value  $\frac{1}{3}$  used by Walden, and not the value of  $\frac{1}{2}$  predicted by Debye and Hückel's theory.

<sup>19</sup> *Trans. Faraday Soc.*, 1927, **23**, 404.

<sup>20</sup> *Amer. Chem. J.*, 1908, **40**, 558.

<sup>21</sup> *J. Chem. Soc.*, 1910, **97**, 1261.

<sup>22</sup> *Z. physik. Chem.*, 1906, **54**, 137.

<sup>23</sup> *J. Chim. Physique*, 1908, **6**, 545.

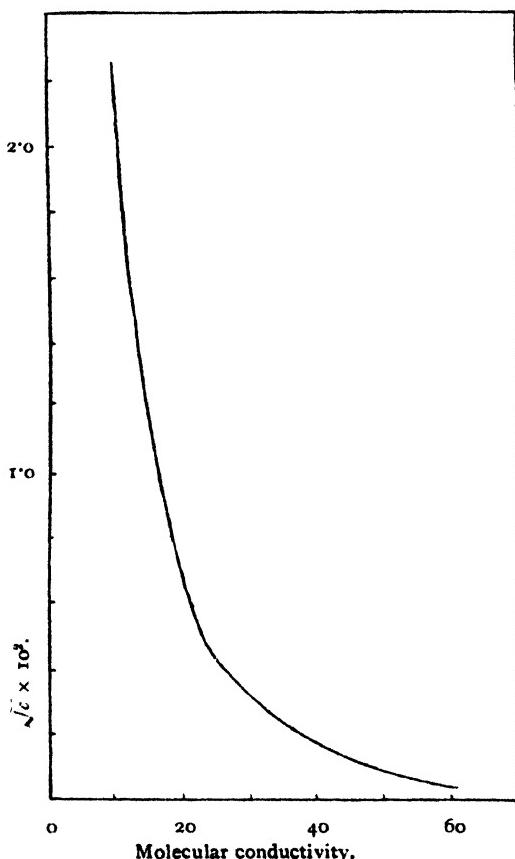


FIG. 5.

## 530 THE DECOMPOSITION OF HYDROGEN PEROXIDE

Hartley and Bell<sup>24</sup> claim that solutions of potassium iodide in alcohol follow the square root law, and give a value for the ionic radius of  $3.26 \times 10^{-8}$  cms. They use the conductivity measurements of Dutoit and Rappeport,<sup>25</sup> who give  $\Lambda_0 = 45$ . As this figure has been exceeded at measurable concentrations by two different workers, any calculations based upon it are doubtful.

### Summary.

The solubilities of potassium iodide in alcoholic solutions of sodium and magnesium iodides of various concentrations have been measured. At concentrations below  $0.5N$  the solubility in sodium iodide + alcohol solutions can be represented by the equation

$$-\frac{1}{2} \log A.P.R. = 3a(\sqrt{2\mu} - \sqrt{2\mu_0}) + \beta c.$$

In the case of magnesium iodide + alcohol solutions evidence for the formation in solution of the complex  $MgI_2 \cdot KI$  is given, and values of the "ionic radius" for each series of solutions are calculated. The scope of this work is to be extended to heterionic solutions.

Measurements have been made of the conductivities of potassium and magnesium iodide solutions, and an equation has been found to represent the results for potassium iodide.

The thanks of the authors are due to the Chemical Society for a grant which covered part of the cost of the materials, and to the Department of Scientific and Industrial Research for a maintenance grant which has enabled one of us (F. S. H.) to finish the work.

<sup>24</sup> *Trans. Faraday Soc.*, 1927, **23**, 399.

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## ON THE DECOMPOSITION OF HYDROGEN PEROXIDE AT SURFACES.

By W. M. WRIGHT AND ERIC K. RIDEAL.

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The experiments of Elissaoff,<sup>1</sup> as well as the more recent ones of Rice,<sup>2</sup> have shown that hydrogen peroxide in dilute aqueous solution undergoes catalytic decomposition at a variety of solid surfaces. Gurwitch indeed traced a rough parallelism between the extent of adsorption of benzoic acid and the rate of catalytic decomposition. Small traces of acids or alkalis, however, affect the rate of decomposition of hydrogen peroxide at various surfaces to a marked extent. The effect of addition of traces of acids or alkalis on the reaction rate is, however, by no means identical for different surfaces, thus acids increase the reaction velocity on normal sugar charcoal and kaolin whilst alkalis effect an increase on glass and ferric oxide. This investigation was carried out with the object of finding an adequate explanation for this apparently anomalous behaviour.

<sup>1</sup> *Z. Elektrochem.*, **21**, 353, 1915; Gurwitch, *Z. physik. Chem.*, **107**, 1923.

<sup>2</sup> *J. physical Chem.*, **31**, 1352, 1507, 1927, and Williams, *Trans. Faraday Soc.*, **24**, 245, 1928.

On immersion of a solid in water an adsorption or electrokinetic potential is generated at the solid-liquid interface. This electrokinetic potential is brought into existence by the so-called Helmholtz double layer formed either by surface ionisation of the solid or by selective adsorption of excess of an ion of one sign from the solution if that contains an electrolyte. A non-electrolyte, if also present in the solution, will be adsorbed as well and may affect the electrokinetic potential by altering the relative ionic adsorptions; the greater the electrokinetic potential in general the smaller the adsorption of the non-electrolyte, this being displaced by the ions. Thus the adsorption of a non-electrolyte will be at a maximum at the isolectric point. The experiments of Frumkin<sup>3</sup> may be cited as proof of this generalisation. We might anticipate that since hydrogen peroxide is an extremely weak acid ( $k = 1.210^{-12}$ ), it exists in solution chiefly as non-dissociated molecules and that the adsorption of hydrogen peroxide would be at a maximum at the iso-electric point of the surface present. Since the peroxide decomposition is in many cases at least a heterogeneous reaction the rate of reaction if unaffected by the electrokinetic potential will be at a maximum at the isolectric point of the surface.

This hypothesis was tested for a number of solid catalysts having iso-electric points ranging from strongly alkaline to strongly acid solutions, and a fair agreement was found between the amount of alkali or acid which must be added to give the maximum rate of decomposition, and that required to neutralise the electrostatic charge on the surface.

The reaction was followed by measuring the rate of evolution of oxygen in a Barcroft differential manometer. The glass vessels were steamed out before use; 0.2 grams of the catalyst was weighed out into a centrifuge tube, and 10 c.c. of the solution of acid or alkali added and the mixture shaken for ten minutes. The solution was then removed by centrifuging and the operation repeated twice. The catalyst and one c.c. of the solution was then transferred to the reaction vessel, and the centrifuge tube washed out with another 1 c.c. of solution; 1 c.c. of a 0.3*N* solution of pure hydrogen peroxide prepared from Merk's Perhydrol was added, making the concentration of H<sub>2</sub>O<sub>2</sub> in the vessel 0.1*N*.

An equal amount of H<sub>2</sub>O<sub>2</sub> solution was placed in the compensating vessel to correct for the slight decomposition which takes place on the walls of the vessel.

<sup>3</sup> *Nature*, 117, 790, 1926; Frumkin and Obrutscheva, *Biochem. Zeit.*, 1927, 182, 220.

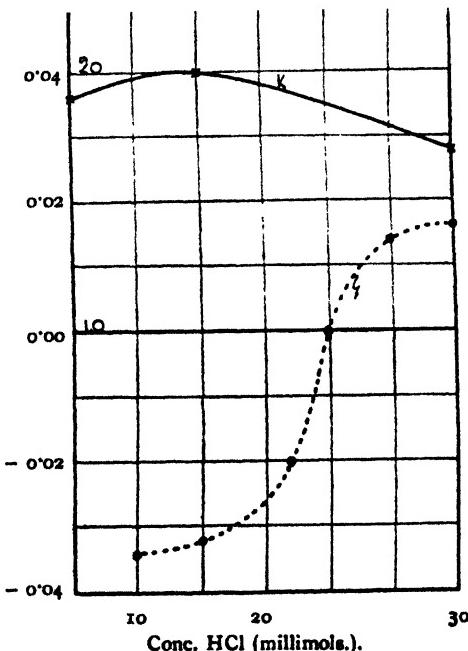


FIG. 1.—Normal sugar charcoal.

The rates of reaction for varying acid and alkali concentrations are shown in Figs. 1-9. In Figs. 1-6 and 9, the scale of  $\zeta$  (in volts) is shown to the left of the Figure and the scale of  $k$  (in c.c. of  $O_2$  per hour) is within the squared lines. It will be seen that there is a certain optimum concentration at which the decomposition velocity is at a maximum.

The electrokinetic potential was determined by the electro-endosmotic method. The apparatus used is shown in the diagram (Fig. 9). A small plug of glass wool was introduced into the lower end of the vertical tube which was then closed with a rubber tube and spring-clip; air-free water was introduced into the vessel and the catalyst, which had been boiled with water, was added. It was left standing for twenty-four hours, after which about a litre of distilled water was drawn through by means of a pump. With most substances the glass wool plug could then be withdrawn, leaving

a compact column of the catalyst, but with charcoal, it was necessary to leave the small plug in position in order to keep the column intact. The solution of acid or alkali of required strength was then introduced and drawn through the column until the concentration of the emerging fluid was the same as that of the original solution. The whole apparatus was then filled with the solution and set up as in Fig. 10. The vertical tube was immersed in a further quantity of the solution in a beaker. The latter was connected with an agar bridge (containing 5 per cent. agar saturated with potassium

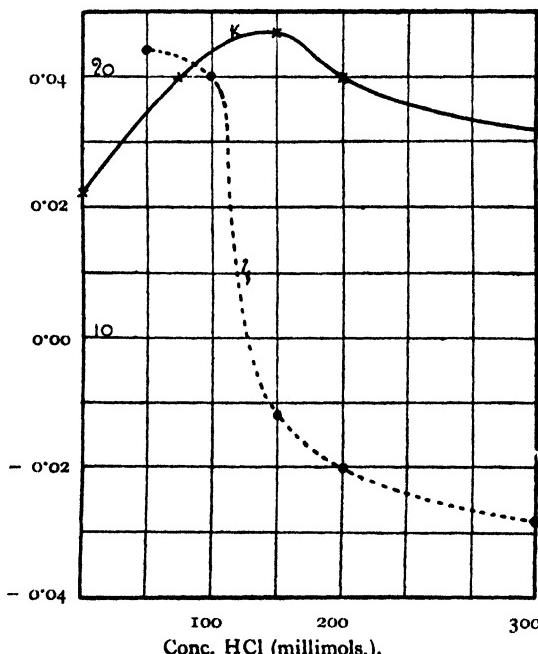


FIG. 2.—Active sugar charcoal.

chloride) to a beaker containing  $N/10$  copper sulphate, a copper wire connected this beaker with a resistance box and one pole of the electrical supply. The other pole was connected by a copper wire to another beaker containing copper sulphate, and then by means of an agar bridge to the top of the catalyst diaphragm. The left side-tube was then joined by a rubber connection to a horizontal capillary pipette graduated in 0.01 c.c. The right side-tube was connected to a reservoir containing the solution of acid or alkali. The apparatus was completely filled with the solution and the level of fluid in the pipette adjusted to zero, the tap connecting the reservoir was then closed. The current was applied and its direction reversed every two minutes, the movement of the fluid in the capillary tube being timed with a stop-watch. The effect of gravity tended to make the movement of fluid towards the right too fast, and the heat produced by the current accelerated the movement towards the left, by

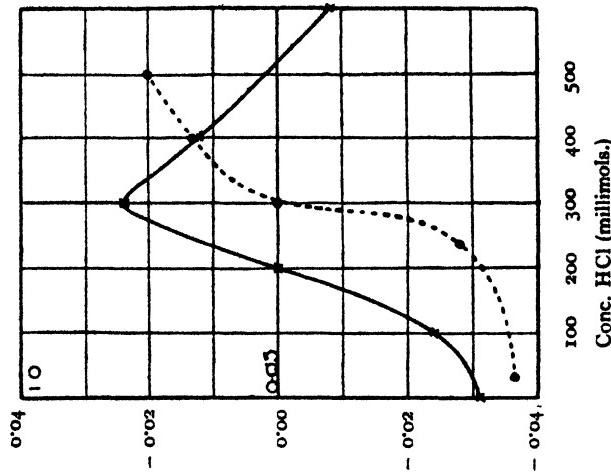
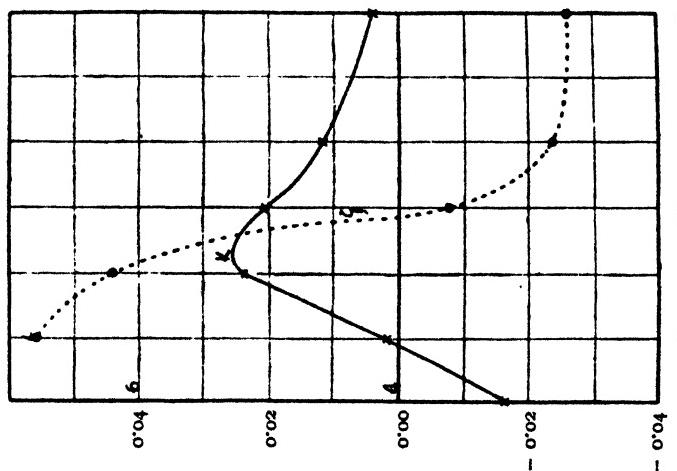
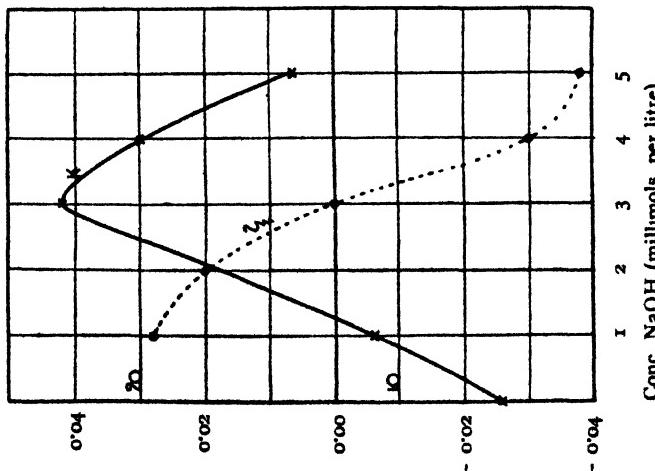


FIG. 5.—Kaolin.

FIG. 4.— $\text{Mg}(\text{OH})_2$ .FIG. 3.— $\text{Fe}_2\text{O}_3$ .

taking the mean of the velocities in both directions the errors due to these effects were eliminated. The potential across the column was measured by means of two supplementary platinum electrodes connected with a potentiometer. Since gas bubbles developed on the platinum surfaces, these electrodes were only introduced after the readings of the velocity of the

movement of the fluid had been taken. The ratio of the effective length  $l$ , of the column to its effective cross-section  $q$  was measured by a method described by Fairbrother and Mastin.<sup>4</sup> The diaphragm was filled with  $N/10$  potassium chloride and a current passed through it, and through a large known variable resistance in series with it. The fall of potential across the diaphragm and across the resistance was measured by means of a potentiometer.

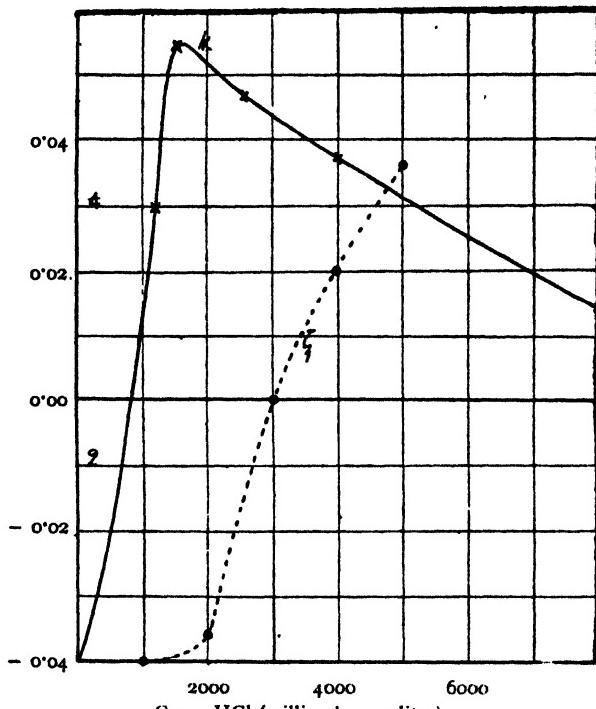


FIG. 6.—Tungstic acid.

This gave from Ohms law the current  $c$  flowing through the diaphragm, then if  $E$  be the potential across the diaphragm,  $C = E \cdot K \cdot \frac{c}{l}$  or  $\frac{c}{l} = \frac{C}{EK}$  where  $K$  is the specific conductivity of  $N/10$  KCl. The electrokinetic potential  $\xi$  is then calculated from the formula

$$\xi = \frac{u \cdot l \cdot 4\pi\eta}{E \cdot q \cdot D}$$

where

$u$  = amount of liquid transported in unit time.

$E$  = potential difference across the diaphragm.

$\eta$  = viscosity of water = 0.01006.

$D$  = dielectric constant of water = 80.

$l$  = ratio effective length to cross-section of diaphragm.

The results are given in the diagrams (Figs. 1-6). The isoelectric point of various catalysts and the concentration of solution at which the rate of

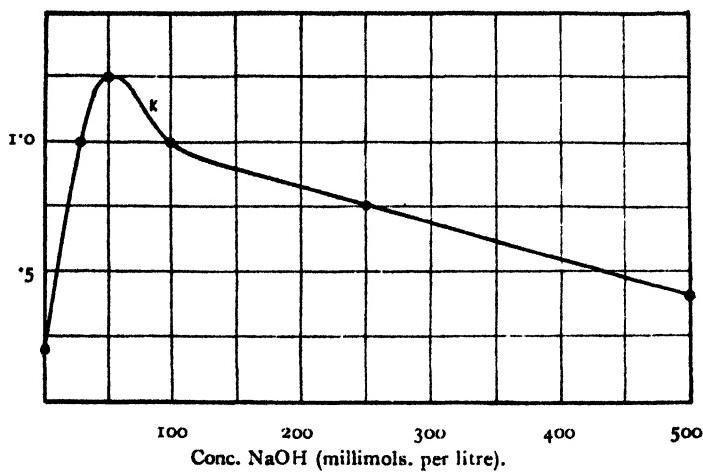


FIG. 7.—Glass.

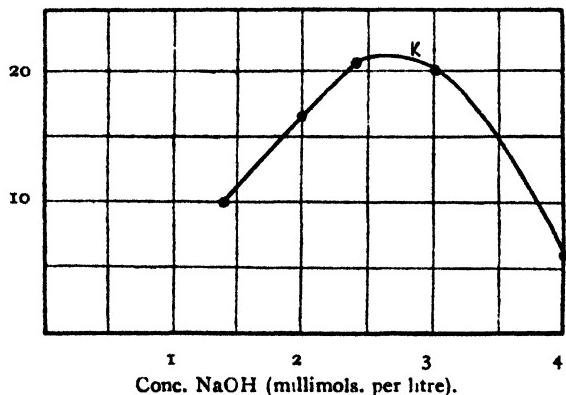


FIG. 8.—ZnO.

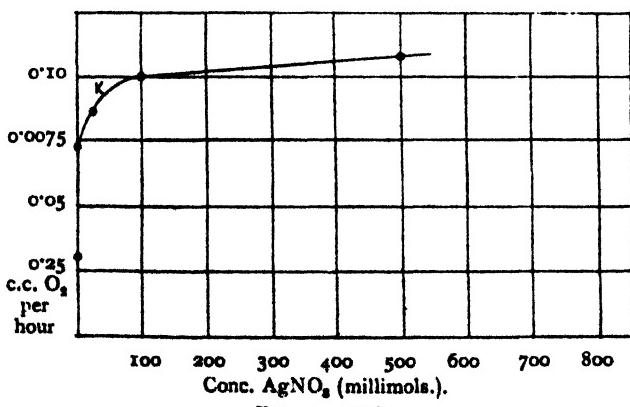


FIG. 9.—AgCl.

decomposition of hydrogen peroxide is at a maximum are given in the following table :—

Catalyst.	Concentration for Maximum Velocity.	Isoelectric Point.
Normal sugar charcoal	0·001 N HCl	0·002 N HCl
Activated sugar charcoal	0·19 N NaOH	0·14 N NaOH
Ferric oxide	0·003 N NaOH	0·003 N NaOH
Magnesium hydroxide	0·005 N NaOH	0·007 N NaOH
Kaolin	0·125 N HCl	0·150 N HCl
Tungstic acid	1·5 N HCl	2·3 N HCl
Glass	0·1 N NaOH	0·1 N NaOH
Chromic chloride	·0008 N NaOH	[·001 N NaOH]
Zinc oxide	·00025 N NaOH	[·003 N NaOH]
Silver chloride	No catalytic activity in acid solution	[·001 N HCl]
Silica gel	" " " "	[·5 N HCl]

The figures in brackets are taken from the literature and can only be considered as approximate values in the present case, since the isoelectric point of a substance varies with the method of preparation and its state of division. Tungstic acid is slowly attacked by hydrogen peroxide forming a soluble pertungstic acid, this may account for the observed discrepancy between the concentration of maximum velocity and the isoelectric point.

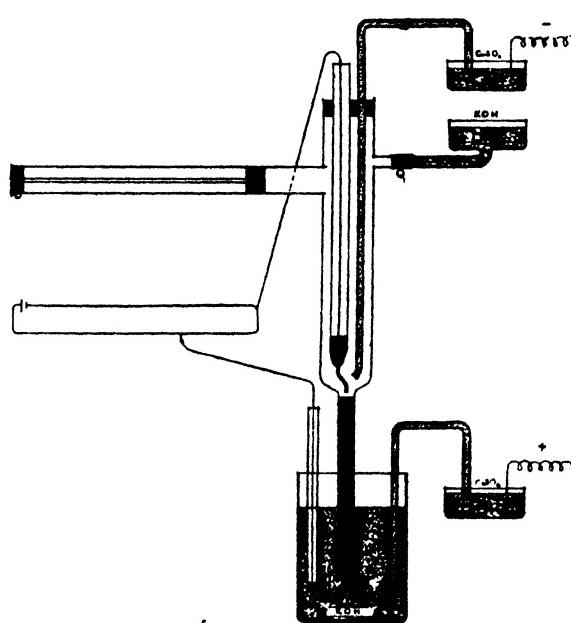


FIG. 10.

The table shows that with most substances examined there is a fair agreement between the concentration of solution at which the velocity of decomposition of hydrogen peroxide is at a minimum and that at which the surface of a catalyst is electrically neutral. Since the maxima are not very clearly defined and the decomposition velocities are only reproducible within about 5 per cent. with many of the catalysts, it is un-

certain whether the true maximum accurately coincides with the isoelectric point, or is slightly displaced. Since, as has been observed, hydrogen peroxide is a weak acid having a dissociation constant of  $1\cdot2 \times 10^{-12}$ , it is possible that its adsorption maxima occur slightly to the alkaline side of the isoelectric points.

It will be observed that whilst in general the rates of decomposition are

at definite maxima at the isoelectric points of the surfaces, at the same time each surface exerts a specific catalytic effect. The alteration in the electrokinetic potentials in the above series of experiments has been effected by ions common to the composition of the surfaces, *viz.*, the oxonium and hydroxyl ions. The electrometric potentials can of course be readily affected by other ions especially the polyvalent ions, and it is to be anticipated that two effects may be observed on the addition of strongly adsorbed ions. As the surface approaches the isoelectric point a change in the extent of adsorption of the hydrogen peroxide occurs, and unless the catalytic activity of the newly-formed surface is markedly different from that of the original when brought to the isoelectric point by a common ion, there will be an increase in the catalytic activity. At high concentrations both ions are adsorbed and the adsorbed salt may poison the active surface.

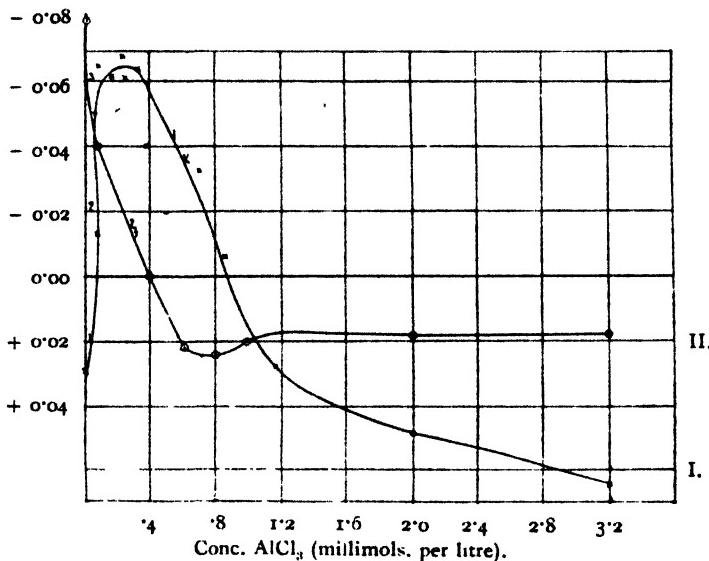


FIG. II.

These two effects are clearly brought out in the behaviour of aluminium chloride.

Powis<sup>5</sup> showed that on addition of very small quantities of aluminium chloride, the potential of glass fell rapidly from -0.08 volts to zero, and on further addition of the salt became positive, reaching a maximum at a certain concentration, and then falling to a small positive value, which remained constant on further addition of aluminium chloride. The actual potential of the glass for any concentrations of this salt is always less than that of glass in pure water. At very low concentrations of the salt, there is a marked acceleration of the decomposition velocity, since the effect due to the lowering of the surface potential is greater than that due to the poisoning of the surface as shown in Fig. II, curve I. The maximum is not very well defined, but appears to exist at a rather lower concentration than the isoelectric point of the glass as determined by Powis, whose data are reproduced in curve II. It is possible that the potential of the glass used differs from that used by Powis, but since the results obtained were

<sup>5</sup> Z. physik. Chem., 89, 91, 1915.

rather irregular, it did not appear worth while to determine the isoelectric point of this glass. At concentration of aluminium chloride greater than 2 millimols per litre the rate of decomposition is less than that in pure water whilst at 8 millimols per litre the catalyst is completely poisoned.

The effect of addition of silver ions to silver chloride is shown in Fig. 9.

**The fraction of the surface which is catalytically active.** Since it has been shown<sup>6</sup> that only part of a charcoal surface is active for the oxidation of oxalic and other acids, it seemed of interest to find out whether the same area alone was active for the decomposition of hydrogen peroxide. Poisoning with capillary active substances showed that the area active for the decomposition was from 3 to 4 times as great as that active for the oxidation as shown in the following table:—

ACTIVE SUGAR CHARCOAL.

Poison.	Per Cent. Poisoning.		
	I. Decomp. H <sub>2</sub> O <sub>2</sub> .	II. Oxidation Oxalic Acid.	Ratio II I.
$\frac{1}{2}$ saturated solution of pelargonic acid	11.7	46.7	4.0
$\frac{1}{2}$ saturated solution of octyl alcohol	25.1	83.3	3.3

since about a third of the charcoal surface is active for the oxidation of oxalic acid, it appears that practically the whole surface is active for the decomposition of hydrogen peroxide, but since the poisons are not absolutely selective on the active areas (*cf.* Wright, *loc. cit.*) these are probably smaller than is indicated by the above data. The experiments show, however, that the surfaces active for the two reactions are not identical.

### Summary.

The rate of surface decomposition of hydrogen peroxide has been studied for a number of surfaces. It is shown that addition of alkalis or acids affect the rate of decomposition and that the maximum rates of decomposition are obtained in accordance with theoretical anticipation at a  $\rho_H$  coincident with that required to bring the surface to its isoelectric point. Tungstic acid shows certain abnormalities, probably associated with the formation of a soluble pertungstic acid. The alteration in reaction rate can likewise be effected by the addition of polyvalent ions such as AlCl<sub>3</sub>. At high concentrations the effects of poisoning by the adsorbed salt can be observed. The fraction of the surface of charcoal capable of effecting the decomposition is much larger than that capable of effecting oxidation of organic acids.

<sup>6</sup> Rideal and Wright, *J. Chem. Soc.*, 1925, 127, 1347; 1926, 1813, 3182, Wright, 1927, 2323.

# THE THERMAL DECOMPOSITION OF HYDROGEN PEROXIDE.

By W. M. WRIGHT.

Received 15th August, 1928.

In a previous communication<sup>1</sup> it was shown that the rate of decomposition of hydrogen peroxide on glass powder in the presence of silver nitrate was approximately proportional to the amount of silver adsorbed; but the experimental results gave no indication as to the form of the silver which is catalytically active. Since the silver ion has no appreciable effect on the velocity of decomposition of hydrogen peroxide, it appeared of interest to investigate further the nature of the adsorbed silver.

Devaux and Aubel<sup>2</sup> showed that glass which has been cleaned with acids behaves like a gel, in that salts in solution are slowly adsorbed into the bulk of the glass, as well as on the surface. The work of Frazer, Patrick, and Smith<sup>3</sup> on the adsorption of water vapour also shows that the surface of glass which has been treated with acids is partially converted into silica gel. It appeared possible, therefore, that with glass in contact with silver nitrate, a small quantity of silver silicate was formed on the surface, and that this acted catalytically on the decomposition of hydrogen peroxide. In order to test this assumption, a study of the rate of decomposition of H<sub>2</sub>O<sub>2</sub> on silica gel and on silver silicate was made.

## I. The Decomposition of Hydrogen Peroxide on Silica Gel.

The silica was prepared from Patrick silica gel. It was ground down and passed through an 80-mesh sieve, and then extracted with hydrochloric acid in a Soxhlet apparatus for six hours, after which it was extracted for two hours with water heated at low red heat in a silica crucible for one hour, and again extracted with water and dried. The product was tested for the presence of iron and other heavy metals; all tests were negative, but the catalytic action of the gel was very irregular, the velocity of decomposition of H<sub>2</sub>O<sub>2</sub>, which was followed by measuring the oxygen evolved in a Barcroft differential manometer, varying by about 20 per cent. The gel was therefore peptised by boiling with dilute alkali for five hours and reprecipitated with hydrochloric acid. It was then washed with water, dried at red heat as before, the process being repeated three times. The product then behaved in a fairly regular manner.

In neutral and acid solution, the silica gel showed no appreciable catalytic activity for the decomposition of hydrogen peroxide. Komarousky<sup>4</sup> has shown that if silica gel is heated with a 30 per cent. solution of hydrogen peroxide, a persilicate is formed having the composition H<sub>2</sub>SiO<sub>4</sub>. 1·5H<sub>2</sub>O, or H<sub>2</sub>SiO<sub>3</sub> · H<sub>2</sub>O<sub>2</sub> · 0·5H<sub>2</sub>O. This product is unstable, and slowly evolves ozonised oxygen, so that with a concentrated solution of the peroxide at high temperatures, silica appears to have a certain catalytic activity, but under the conditions of the present work [N/20 . H<sub>2</sub>O<sub>2</sub> at 20° C.] any decomposition due to the reaction with the silica was much less than that

<sup>1</sup> Z. Elektrochemie, 34, 298, 1928.

<sup>3</sup> J. Physical Chem., 31, 897, 1927.

<sup>2</sup> Compt. rend., 134, 601, 1927.

<sup>4</sup> Chem. Zeit., 38, 121, 1914.

taking place on the walls of the vessel. In alkaline solution the gel showed a slight catalytic action reaching a maximum in about  $0.001\text{N}$ . NaOH.

There is also a slight activity in the presence of calcium chloride and of aluminium chloride. The reaction velocity with these salts is given in the following table:—

Catalyst.	K. c.c. O <sub>2</sub> Per Gm. Gel Per Hour.
Silica gel + water . . . .	0.03
" " + 0.005 NaOH . . . .	0.04
" " + 0.01 NaOH . . . .	0.05
" " + 0.05 . . . .	0.05
" " + 0.05 CaCl <sub>2</sub> . . . .	0.05
" " + 0.05 AlCl <sub>3</sub> . . . .	0.06

A very marked acceleration of the rate of decomposition occurred in the presence of small concentrations of silver nitrate as shown in the figure.

On addition of  $0.0001\text{N}$  NaOH the rate of decomposition is increased some 500 times, this velocity was too fast to be measured accurately in the Barcroft apparatus, but a further addition of  $0.001\text{N}$  NaOH did not appear to have much effect on the oxidation velocity.

The adsorption of silver nitrate on the gel was very small, being less than 0.005 millimols per gram of gel in contact with a 0.5 molar AgNO<sub>3</sub> solution. On addition of  $0.001\text{N}$  NaOH, the adsorption of silver nitrate at once increased to about 0.5 millimols, further addition of alkali up to  $0.005\text{N}$  NaOH did not appreciably increase the absorption of the silver, the silica appearing to act as a buffer within this range.

This buffer effect was shown by measuring the  $p_H$  of solutions in contact with the gel; they were compared with buffer solutions made from mixtures of citric acid and disodium hydrogen phosphate, using azolitmin as an indicator. The silica in contact with the  $0.05\text{M}$  silver nitrate solution maintained the solution at  $p_H$  7.2 in the presence of NaOH from 0.001 to  $0.005\text{M}$  as shown in the following table:—

(1) SILICA GEL IN CONTACT WITH ALKALI.

Conc. NaOH . . . .	0	.001	.002	.003	.004	.005
$p_H$ . . . .	6.9	7.2	7.3	7.4	7.6	8.0

(2) SILICA GEL IN CONTACT WITH 0.05 MAg NO<sub>3</sub> + ALKALI.

Conc. N..OH . . . .	0	.001	.002	.003	.004	.005
$p_H$ . . . .	6.9	7.2	7.2	7.2	7.2	7.2

## II. The Decomposition of Hydrogen Peroxide on Silver Silicate.

The salt was made by the action of silver nitrate on sodium silicate prepared from the pure silica gel. After washing for two hours with hot water, the silver silicate still contained a small quantity of adsorbed silver nitrate, but since the latter is not a catalyst, the activity of the salt is probably not greatly affected by this impurity. Silver silicate is decomposed by all acids; it was light brown when first formed but darkened on keeping, probably owing to partial decomposition by the CO<sub>2</sub> of the air.

On addition of hydrogen peroxide the salt immediately turned black, and a very rapid evolution of oxygen occurred. On addition of dilute nitric acid, the black colour disappeared, and the evolution of oxygen ceased. A light brown product was left. On addition of dilute sodium hydroxide the decomposition again proceeded rapidly, the solid turning black as before. The reaction may probably be explained as follows :—

The hydrogen peroxide decomposes the silver silicate forming persilicic acid and silver oxide, the latter then reacts with the hydrogen peroxide, with the evolution of oxygen and the formation of silver suboxide, the latter then acts as a catalyst for the decomposition.

No peroxide of silver could be detected in the solution.

That the active catalyst is an oxide of silver and not the metal, is indicated by the results of some experiments on sheet silver. With a clean metal surface produced by polishing or with a fresh-cut surface the rate of decomposition of hydrogen peroxide was very slow. If, however, the silver was previously cleaned with nitric acid and then washed with water until the acid had been completely removed, a very active catalyst was produced, probably owing to the formation of an oxide of silver. The velocity of decomposition of hydrogen peroxide on this surface was not affected by the presence of hydroxyl ions in solution, as shown in the following table :—

Conc. KOH [millimols per litre]	0	3	6	12	24	240
Velocity [c.c. O <sub>2</sub> per mgm. per hr.]	15·2	14·7	15·0	15·4	14·8	15·0

The increase in velocity of decomposition of H<sub>2</sub>O<sub>2</sub> with glass and silver nitrate in the presence of alkali is thus probably due to the formation of silver oxide.

In order to compare the rates of decomposition on silver silicate with that of silica in contact with silver nitrate, the silver silicate was mixed with 250,000 times its weight of silica and the velocity of decomposition of hydrogen peroxide by this mixture determined.

One gram of this powder containing 0·004 mgm. of silver silicate gave a decomposition rate 2·4 times as fast as that produced by one gram of silica in contact with 0·05*N* silver nitrate. Therefore if the catalytic activity of the latter is due to the formation of silver silicate, the concentration of the latter on the surface is 0·00167 mgm. or 9·1 × 10<sup>-6</sup> millimols per gram.

In order to compare the catalytic activity of the silica gel with that of the Jena glass used in the previous experiments,<sup>1</sup> it is necessary to know the specific surfaces of these two substances. An attempt was made to estimate the surface of the powders from the adsorption maximum of methylene blue.<sup>5</sup> The glass powder gave a maximum adsorption of the dye corresponding to an area of about 0·018 sq. m. per gram, the silica gel, however, adsorbed the dye very feebly and gave no definite maximum in neutral solution. On addition of 0·01*N* KOH, a great increase in adsorption of the methylene blue on the silica occurred, giving a maximum of 54·6 sq. m. per gram, while the adsorption on the glass was only slightly increased, the maximum in 0·01*N* KOH being 0·20 sq. m. per gram. Further addition of alkali did not sensibly increase the adsorption of methylene blue on either silica or glass. It may therefore be taken that the ratio of the specific surfaces of these two substances are as 0·02 : 54·6 = 1 : 2700

<sup>1</sup> Cf. Paneth and Radu, *Ber.*, **57**, 1221, 1924.

The catalytic activity per gram of the two substances is of the same order of magnitude, that on glass being 0.13 c.c. O<sub>2</sub> per gram per hour and that of silica being 0.04 in the same units. In the presence of 0.01*N* KOH, the rate on glass K = 0.20 and on silica K = 0.19 c.c., O<sub>2</sub> per gram catalyst per hour. That is, in alkaline solution the rate per sq. cm. of surface is nearly 3000 times as fast on glass as on silica. This effect may be attributed to the salts of calcium, iron, etc., present in the glass.

If now we compare the adsorption of silver nitrate on both substances we find that whereas the adsorption on silica gel is immeasurably small, that on glass is quite appreciable, and follows the usual exponential adsorption isotherm.<sup>1</sup> Yet on comparison of the rate of decomposition of hydrogen peroxide on glass in contact with silver nitrate with that on silver silicate, it follows that only an exceedingly small fraction (less than  $\frac{1}{100000}$ ) of the total adsorbed silver can be present as silver silicate on the surface; the rest is probably adsorbed as unchanged silver nitrate which has no catalytic activity. If minute patches of silica gel are distributed irregularly over the glass surface and if there is no preferential adsorption of the silver nitrate on these patches, then the amount of silver silicate formed for low concentrations of silver nitrate will be approximately proportional to the total amount of silver adsorbed, as indicated by the experimental data.

### Summary.

1. Pure silica gel has only a slight catalytic activity for the decomposition of hydrogen peroxide. This activity is greatly increased in the presence of silver nitrate. The addition of a trace of alkali increases the activity with the silver salt several hundred times.

2. The adsorption of silver nitrate on the gel is very small, but is considerably increased on addition of a trace of alkali. Further addition of alkali up to 5 millimols per litre does not increase further the adsorption of silver, the system exerting a buffer action over this range.

3. Silver silicate causes a very rapid decomposition of hydrogen peroxide, and is itself decomposed to an oxide of silver which is catalytically active.

4. Clean sheet silver is a very feeble catalyst, but if previously cleaned with nitric acid, it becomes very active probably owing to the formation of an oxide of silver. Its activity is unaffected by the concentration of hydroxyl ions in solution.

5. The catalytic properties of glass in contact with silver nitrate may be ascribed to the formation of traces of silver silicate. Less than  $\frac{1}{100000}$  of the total adsorbed silver is present in this form.

I wish to express my best thanks to Dr. E. K. Rideal for his interest and advice in connection with this work.

# ON THE VAPOUR PRESSURES OF BINARY SYSTEMS; THE AQUEOUS SOLUTIONS OF ORTHOPHOSPHORIC ACID, SODIUM HYDROXIDE, AND POTASSIUM HYDROXIDE.

By UKITIRO NAKAYA.\*

*Received 20th August, 1928.*

In this paper aqueous solutions of orthophosphoric acid, sodium hydroxide and potassium hydroxide are examined on the line of Professor A. W. Porter's papers on binary mixtures.<sup>1</sup> Special care has been taken to include sufficient terms to represent all the known characteristics of the experimental vapour pressure curve. This equation seems to fit the experimental data well and also stands some extrapolation. The case of orthophosphoric acid described below is an example where no saturation occurs.

The experimental data made use of are those of Tammann in the tables of Landolt and Börnstein. The vapour pressures given are those corresponding to a temperature of 100° C. The molar fractions at any concentration are represented by  $\mu_1$  for water and  $\mu_2$  for solute. The values calculated from the data are as follows:—

H <sub>3</sub> PO <sub>4</sub> .		NAOH.		KOH.	
$\mu_1$ .	$a_1$ .	$\mu_1$ .	$a_1$ .	$\mu_1$ .	$a_1$ .
.963	.960	.992	.988	.992	.982
.962	.959	.987	.978	.984	.966
.924	.906	.966	.938	.980	.955
.903	.868	.948	.896	.973	.935
.852	.759	.936	.875	.969	.927
.785	.617	.908	.791	.959	.900
.712	.467	.905	.763	.955	.890
.669	.384	.888	.730	.947	.865
.623	.332	.872	.673	.936	.830
		.851	.598	.914	.749
		.828	.523	.879	.613
		.743	.404	.860	.528
		.748	.285	.840	.465
				.833	.442
				.808	.360

The following equations are of permissible form and satisfy the experimental data all over the regions determined:—

$$\text{H}_3\text{PO}_4, \log a_1 = \log \mu_1 + 1.63 \mu_2^2 - 9.98 \mu_2^3 (1 + 3\mu_1) + 6.94 \mu_2^4 \\ (1 + 4\mu_1 + 10\mu_1^2)$$

$$\text{NaOH}, \log a_1 = 1.7 \log \mu_1 - 2.28 \mu_2^2 - 4.25 \mu_2^3 (1 + 3\mu_1)$$

$$\text{KOH}, \log a_1 = 2.1 \log \mu_1 - 4.16 \mu_2^2 - 3.76 \mu_2^3 (1 + 3\mu_1).$$

\* Communicated by Professor Alfred W. Porter, F.R.S.

<sup>1</sup> *Trans. Faraday Soc.*, 24 (1928), 343, 405, 407.

The experimental data are shown as circles, crosses, and dots respectively in Fig. 1. The above curves, calculated for the whole range of values of  $\mu_1$ , are drawn as continuous lines. They have the following properties :—

(1) In the case of  $H_3PO_4$  the curve shows some tendency toward instability as described in Professor Porter's paper. As orthophosphoric acid, however, can be mixed with water in any proportions we cannot expect such region, and in agreement with this the equation also just fails to show any saturation point. The curve has an inflection point at  $\mu_1 = \mu_2 = 0.5$ , and it seems to repeat the same kind of changes at  $\mu_1 = 0.5$  as at  $\mu_1 = 1.0$ . This may perhaps be taken as indicating that a loose compound of  $H_3PO_4 \cdot H_2O$  is formed in the solution.

(2) In the case of sodium hydroxide or potassium hydroxide the vapour pressure decreases rapidly with the increase of concentration and tends to

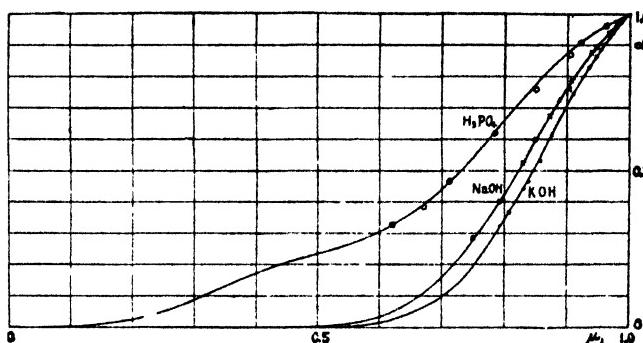


FIG. 1.

nil practically at  $\mu_2 = 0.5$ . The interpretation may be that beyond  $\mu_2 = 0.5$  all water molecules "combine" with the solute and thus show no sensible vapour pressure. In the case of potassium hydroxide at  $100^\circ C.$ , a 64.6 per cent. solution is in equilibrium with  $KOH \cdot H_2O$ . We might expect, therefore, the curve to have a horizontal tangent at that point, *i.e.*, at  $\mu_2 = 0.39$ . The dissociation pressure of  $KOH \cdot H_2O$ , however, is not negligibly small, having a value of 1.54 mm. at  $27.75^\circ C.$  and 2.12 mm. at  $31.75^\circ C.$  In such a case when the dissociation pressure is comparable with the supposed vapour pressure of solution a further discussion of this equation will be needed.

The hearty thanks of the author are given to Professor A. W. Porter for his kind advice and guidance.

*The Faraday Society is not responsible for opinions expressed before it by  
Authors or Speakers.*

A GENERAL DISCUSSION  
ON  
**HOMOGENEOUS CATALYSIS**

HELD IN THE PHYSICAL CHEMISTRY LABORATORY OF THE UNIVERSITY  
OF CAMBRIDGE, ON FRIDAY AND SATURDAY, 28TH AND 29TH  
SEPTEMBER, 1928.

PROFESSOR C. H. DESCH, D.Sc., F.R.S. (PRESIDENT) IN THE CHAIR.

**INTRODUCTORY PAPER.**

**SOME PROBLEMS IN HOMOGENEOUS CATALYSIS.**

PROFESSOR T. M. LOWRY.

*Received 16th July, 1928.*

I have been given this opportunity to explain the purpose of the Cambridge Discussion on Homogeneous Catalysis. This is the 50th discussion that has been arranged by the Faraday Society, and the second that has been held in this laboratory. The related problem of heterogeneous catalysis was discussed in London in 1921, and the special group of changes which are catalysed by the action of light was discussed at Oxford in 1925. We have also organised a discussion on the special problems of gaseous explosions, where both homogeneous and heterogeneous catalysis may play an important part. The present discussion may be expected to have as its mass-centre the problems of catalysis by acids and bases, on which a great deal of experimental work has been done since Ostwald first adopted the too-simple view that catalysis by acids is an exclusive property of the hydrogen ion. We have, however, deliberately given to the discussion a much wider scope than this particular aspect of the chemistry of aqueous solutions, and our first two reports necessarily touch on gaseous reactions.

The first report, by Mr. Hinshelwood, raises the question : Are uncatalysed reactions possible in simple systems? Seven years ago, in a discussion on the radiation hypothesis, I questioned the evidence for the existence of a real unimolecular reaction, in view of the fact that even the migration of a hydrogen atom in a labile compound can be arrested by careful purification. Since that time, however, evidence has been brought forward, mainly by Hinshelwood himself, but also by other workers in the same field, to show that complex molecules can be decomposed by heat alone, without the extraneous aid either of heterogeneous or of homogeneous catalysts, as typified by a glass surface and by water-vapour. Since these thermal decompositions are rather brutal, the current view of this problem may perhaps be summarised by saying that the purest sugar can be charred if you heat it enough, and to this proposition we should most of us instinctively assent; but, equally by instinct, we may wonder whether, in the

hands of Professor H. B. Baker, a compound of such relative simplicity as nitrogen pentoxide might not acquire a stability that it does not possess in other laboratories. The present discussion would certainly have justified itself, if it should lead to successful trials in this direction.

Dr. Rideal's report deals with the vexed question of negative catalysis. The phenomenon is well-established, but the explanation is still a matter for discussion. The negative catalyst is often an anti-catalyst, as I know from my own experiments on the arrest of mutarotation in chloroform. In this case the negative catalyst is certainly carbonyl chloride, which acts by hunting down and carbamidizing the basic impurities which are such powerful catalysts for these changes. In other cases, a negative catalyst acts by poisoning the surface of a solid catalyst. This explanation is limited to cases of heterogeneous catalysis; but do we really know that all our homogeneous actions take place in a single phase? One may doubt it in view of the evidence put forward by Dr. Norrish at the last Cambridge discussion to show that even ethylene and bromine will only combine in contact with a polar surface. The possibility of surface catalysis introduces the obvious possibility of surface poisoning as a means of explaining the minuteness of the amounts of stabilisers that may suffice to inhibit chemical change in a reactive compound. Professor Moureu and M. Dufraisse will tell us what they think about this problem in the special fields of oxidation and polymerisation in which they have done so much experimental work.

These general problems are largely concerned with defining the scope covered by the subject of our discussion. We may now pass on to the more specific problems of homogeneous catalysis. In studying the interactions of gaseous molecules we are concerned mainly with *binary* collisions, since *ternary* collisions are much less common. It is therefore customary to analyse a gaseous reaction into a series of steps, each of which involves the collision of only two bodies. This method of analysis has been applied very successfully by Berthoud and others to chemical changes which are initiated by the action of light; but an equal measure of success has been achieved in the case of dark reactions by Backström, Polanyi, and other workers on homogeneous reactions, who are here to give us an account of their work. Of very special interest is the application to such changes of the chain-mechanism, which was first introduced in order to explain the abnormally high quantum-efficiency of some photochemical reactions, and has since been applied to some cases of heterogeneous catalysis, where a chemical change is initiated by a solid catalyst, and spreads from the surface into the interior of a liquid or gaseous phase.

An essential feature of all cases of catalysis is the bringing together of the catalyst and the reactants. Thus, we cannot expect to hydrolyse an ester until the molecule of the ester is coupled up either with a molecule of water, or with its component parts; and, if a catalyst is needed, we must bring it into the scheme, and postulate a ternary contact as an essential feature of the catalysed reaction. Professor Kendal has proved that binary compounds of the three essential components are constantly formed, but the ternary complex has proved much more elusive. This is perhaps inevitable, since Professor Boeseken has pointed out, in his own studies of catalysis (*e.g.* by aluminium chloride in the Friedel-Crafts reaction) that, if the intermediate complex were sufficiently stable to be isolated, it would probably hold up the further transformation of the system, and so cease to be an effective agent of catalytic change.

Before leaving the subject of intermediate compounds, I should like to call attention to a case of homogeneous catalysis, which is of an entirely

different character to the majority of those which have been studied hitherto, namely the mutarotation of optically-active coordination compounds, such as the beryllium and aluminium derivatives of benzoylcamphor. The mutarotation of these compounds is caused by the optical inversion of a dissymmetric atom of beryllium or of aluminium, and in the former case the change is catalysed by acetone and by chloroform. This novel group of catalysts probably includes all those molecules or ions which can enter the inner sphere of the coordination-complex, since the dissymmetry of the molecule depends on the chelate character of the coordinated radicals and disappears when one limb of the claw loses its grip on the central atom. Chloroform, which is an effective agent for this purpose, actually forms with beryllium benzoylcamphor an unstable molecular compound of the required type.

We may now pass on to consider the much-discussed problem of catalysis by acids and bases. The story is a long one, but can be summarised briefly. In the year 1887, when the *Zeitschrift für physikalische Chemie* was founded, Ostwald had already published two series of papers in the *Journal für praktische Chemie* on the measurement of chemical affinity and on chemical dynamics. In these papers he showed that the "affinity-constants" of a series of acids had the same relative magnitude, whatever the nature of the action in which they intervened. In 1884,<sup>1</sup> he made the important announcement that the relative magnitude of the affinity-constants of a series of thirty-four acids, as deduced from experiments on the homogeneous catalysis of the hydrolysis of methyl acetate and of the inversion of cane-sugar, corresponded with the electrical conductivities of the acids. In 1887<sup>2</sup> he showed that the velocities of saponification of ethyl acetate by four alkalis and thirteen nitrogenous bases were related in a similar manner to the conductivities of these bases. These results were in agreement with views which had already been advanced by Arrhenius in 1883, in his thesis on the Conductivity of Electrolytes.<sup>3</sup> When, therefore, the theory of electrolytic dissociation was finally developed in 1887, it was natural to attribute the catalytic activity of the acids and bases to the free hydrogen and free hydroxyl ions in the solutions. Ostwald therefore concluded "that the possibility of taking part in chemical reactions lies only in the free ions, and that consequently the capacity of reaction in a given solution is proportional to the number of free ions it contains."<sup>4</sup>

Arrhenius supported Ostwald's theory by arguing that the repression of catalysis on adding an ammonium salt to ammonia could be interpreted as depending on a repression of the conductivity of the base.<sup>5</sup> Two years later, however, he made the important discovery<sup>6</sup> that, when cane sugar was inverted in presence of nitric acid at 25°, the velocity of inversion increased in the ratio 6·07 : 1 when the concentration was increased in the ratio 5 : 1, from 0·1 to 0·5*N*, whereas the number of hydrogen ions, calculated in the usual way, increased only in the ratio 4·64 : 1. In other words, the catalytic activity of a given weight of acid *increased*, when the coefficient of ionisation *decreased*. Arrhenius,<sup>7</sup> got over this difficulty in a very modern way by assigning to the hydrogen ion an activity  $f(x)$  which increased with the concentration of  $x$  as follows :—

$x$	0·4	0·2	0·1	0·05	0·01	0·005	0·002	0·001	0·0005
$f(x)$	1·29	1·10	1·00	0·95	0·90	0·88	0·85	0·80	0·75

<sup>1</sup> *J. prakt. Chem.*, 1884, 29, 392-401.

<sup>2</sup> *Mem. Acad. Sci. de Suède*, June, 1883.

<sup>3</sup> *Outlines of Theoretical Chemistry*, 1890, p. 360.

<sup>4</sup> *Z. physikal. Chem.*, 1887, 1, 133.

<sup>5</sup> *Ibid.*, p. 246.

<sup>6</sup> *Ibid.*, 1887, 35, 121.

<sup>7</sup> *Ibid.*, 1889, 4, 226.

Ostwald's theory ought really to have fallen to the ground when a device of this kind was needed to reconcile it with facts by which it was so directly contradicted; but "hope springs eternal in the human breast," and there are not a few chemists who appear still to cling to the belief that, if only the right function can be found to express the activity of the hydrogen and hydroxyl ions, it will be possible to restore the monopoly of catalytic action which was assigned to them by Ostwald, and which they are in danger of losing in these ultra-democratic days. It is a mere matter of history to record that, when I first invited the Faraday Society to come to Cambridge, in order to discuss in my own laboratory the problems of homogeneous catalysis, my primary motive was to provide an opportunity for those who hold these views to speak out, and to show us by what process of substitution they propose to explain away the observations by which the catalytic activity of other components of the solutions has been demonstrated, in the first instance by Dawson, but with full support from analogous observations in Professor Brönsted's laboratory in Copenhagen and in my own laboratory in Cambridge.

The alternative view, that the undissociated molecules of an acid have a catalytic action apart altogether from that of the ions, was first stated clearly in 1912 by Snethlage,<sup>8</sup> who gave for the ratio,  $k_m/k_H$ , of the catalytic activity of the molecule of the acid to that of its ions, the value 0·06 for picric acid, and about 2 for hydrochloric acid. This view has since been advocated persistently, as the "Dual Theory of Catalysis," by Professor Dawson,<sup>9</sup> who has given independent values for the ratio  $k_m/k_H$  for several acids. More importance attaches, however, to his more recent proof that the *anion of a weak acid*, and therefore of its neutral salts, can also act as a catalyst. This development is of revolutionary importance, since it is a complete repudiation of the hypothesis of Arrhenius and of Ostwald, that the acceleration produced by a neutral salt can only be an indirect action, resulting from the stimulation to increased activity of the hydrogen (or hydroxyl) ions, to which alone a direct catalytic action is assigned. Dawson will give an account of his own work on the catalysis of the iodination of acetone and of the hydrolysis of ethyl acetate, so I need only add that experiments made in this laboratory, on lines suggested by Dawson's work, have confirmed his results by showing that the acetate ion of sodium acetate is a powerful catalyst for the mutarotation of glucose.<sup>9a</sup> This is true, even when the alkalinity of the sodium salt has been counteracted by the addition of acetic acid, to a point at which the solution is feebly acid and might therefore be expected to have rather less catalytic activity than pure water.

These observations, and a parallel series of experiments by Brönsted and Guggenheim<sup>10</sup> on the changes of volume which accompany these changes of rotatory power, have enabled us to add the *kations of a weak nitrogenous base* to our new list of catalysts. It is, however, a significant fact that *all* the ions and molecules in which catalytic activity has now been detected are either *acids or bases*, in terms of the modern definition<sup>11</sup> which defines an acid as a substance which can give a proton to a base, and a base as a substance which can accept a proton from an acid. A complete solution of our main problem can therefore be found by substituting a newly-defined *acid* for Ostwald's *hydrogen ions*, and a newly-defined *base* for his

<sup>8</sup> Z. Elektrochem., 1912, 18, 539.

<sup>9</sup> J. Chem. Soc., 1913, 103, 2135; 1915, 107, 1426, et seq.

<sup>9a</sup> Lowry and Smith, J. Chem. Soc., 1927.

<sup>10</sup> J. Amer. Chem. Soc., 1927, 49, 2554.

<sup>11</sup> Lowry, Chem. and Ind., 1923, 42, 43; Brönsted, Rec. Trav. Chim., 1923, 42, 718.

*hydroxyl ions.* In making this substitution, however, we are obliged to foreswear the fundamental doctrine of Ostwald's creed, since catalysis is now seen to be effected by *molecules* as well as by *ions*. It cannot therefore be correlated any longer with conductivity, even as a first approximation, unless we deliberately choose conditions in which catalysis by molecules is small as compared with catalysis by ions. For instance, the catalytic activity of a buffer solution depends far more on the concentration of the salts which it contains than on the concentration of hydrogen or hydroxyl ions which it professes to perpetuate; and a perfectly neutral solution may have a catalytic activity far greater than that of neutral water if it contains the neutral salt of a weak acid and a weak base.

The effects produced by these catalysts are proportional to their concentrations over a wide range. This observation is important in view of the fact that other workers, such as Harned, Scatchard and Soper, have obtained a closer proportionality in other cases of homogeneous catalysis, when they replaced the *concentration* of each component by an *activity* deduced from measurements of solubility, vapour pressure or electromotive force. It is, therefore, a matter of interest to discover whether the catalytic coefficients, which have been deduced empirically from these linear relationships, ought to be modified or corrected in order to allow for the difference between the concentrations and the thermodynamic activities of the components. In particular, it is important to know whether we are justified in suspecting that the catalytic activity of an acid or a base is related just as little to its thermodynamic activity as it is to its conductivity. Information on this point would therefore form a very welcome contribution to the present discussion.

We have seen that acids and bases are unique in their ability to promote both hydrolysis and prototropic change; indeed, Rice has gone so far as to hint that all slow organic reactions which are really homogeneous may be assigned to this group of catalysed reactions.<sup>12</sup> It is therefore interesting to enquire how these catalysts exercise their unique ability to promote the chemical changes now under consideration. Ostwald himself, as we have seen, sought to correlate the activity of the catalyst with its electrolytic conductivity; but the substance catalysed was omitted from this scheme, since it was usually a non-electrolyte. The suggestion that the activated form of an ester, like the active part of an electrolyte, consists of ions, was first made in 1900 by Euler,<sup>13</sup> who suggested that the hydrolysis of ethyl acetate depends on its ionisation in accordance with one of the following schemes:



The ionisation of an enol, and the formation of a non-ionisable ketone by recombination of these ions, had, however, already been suggested by Brühl<sup>14</sup> as an explanation of keto-enolic change in ionising solvents. Brühl's theory was untenable, since it postulated a non-reversible change of enol into ketone, but it is of interest as having led to the "Mechanism of Simple Desmotropic Change" which Lapworth suggested in 1902,<sup>15</sup> and which has been revived quite recently by Euler<sup>16</sup> and by Kuhn and Jacob.<sup>17</sup> According to Lapworth's theory "the internal change takes place only in the ion"

<sup>12</sup> "Mechanism of Homogeneous Organic Reactions," 1928, p. 15.

<sup>13</sup> *Z. physikal. Chem.*, 1900, **32**, 348; 1901, **36**, 405 and 641; 1902, **40**, 498; 1904, **47**, 353; *Ber.*, 1900, **33**, 3202; 1901, **34**, 1568.

<sup>14</sup> *Ber.*, 1899, **32**, 2326.

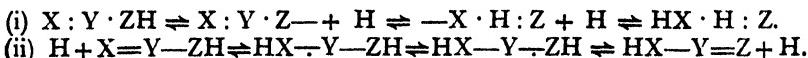
<sup>15</sup> *Trans. Chem. Soc.*, 1902, **81**, 1508.

<sup>16</sup> *Biochem. Z.*, 1920, **170**, 150; *Arkiv. Kemi. Min. Geol.*, 1923, **8**, No. 281.

<sup>17</sup> *Z. physikal. Chem.*, 1924, **113**, 389.

of the organic compound, and the function of the catalyst is to promote the formation of these ions. Thus the catalytic action of a *base* was attributed to the formation of a reactive *anion* by the reversible removal of a hydrogen ion from the organic molecule; and conversely the catalytic activity of an *acid* was attributed to the formation of a reactive *kation* by the reversible addition of a hydrogen ion to the organic compound.

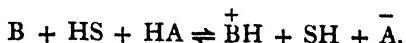
Lapworth's view was therefore expressed by two schemes showing the effect of (i) the reversible *removal* of a hydrogen ion, e.g. by a basic catalyst, and (ii) the reversible *addition* of a hydrogen ion, e.g. by an acid catalyst, as follows :—



In these schemes no electrical charges were shown, but the spare bond in scheme (i) can obviously be replaced by a negative charge, which is neutralised when the hydrogen ion is reattached to the organic radical; and the dot, which was used in scheme (ii) to indicate "the direction in which the 'free affinity' of Y is temporarily disposed," can be replaced by the opposite charges of an electrovalence. The internal change is then (i) a molecular rearrangement of the anion,  $X:Y \cdot \bar{Z} \rightleftharpoons \bar{X} \cdot Y:Z$ , or (ii) the formation of a double bond by the removal of a proton from one of two alternative positions in the kation,  $HX \cdot Y \cdot ZH \rightleftharpoons HX \cdot Y:Z$  or  $X:Y \cdot ZH$ . It will be seen that this mechanism is in complete accord with the recent observations cited above, which show that catalytic activity is characteristic of all types of acid or base, which can either give a proton to the organic compound or accept a proton from it.

These observations were all made with aqueous solutions, and further development was only possible when water was eliminated from the system. The discovery was then made that neither pyridine nor cresol is a complete catalyst for the mutarotation of tetramethylglucose,<sup>18</sup> although pyridine is both a base and an ionising solvent, in which salt-formation in the sense of Lapworth's theory should occur quite freely. A mixture in which the basic and acid properties of the pyridine and cresol are largely neutralised by forming a salt is, however, a far better catalyst even than water itself. This result can only be interpreted on the view that prototropic change depends on the presence of an amphoteric solvent, which can both *give* and *take* a proton. This view is supported by the powerful catalytic activity of weak salts, such as ammonium acetate, in contrast with the complete absence of catalytic activity in salts such as sodium chloride, which can neither give nor accept a proton.

I need not stop to discuss the electrolytic theory of catalysis which I have based on these observations,<sup>19</sup> and which I have discussed more fully in a communication to the forthcoming Paris conference,<sup>20</sup> except to call attention to the very neat method of formulating this group of prototropic changes, which has been used by Brönsted and Guggenheim.<sup>10</sup> These authors write the two prototropic forms of a sugar as HS and SH respectively. The transformation under the combined influence of a base B and an acid HA can then be represented by the scheme

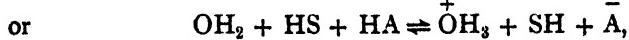
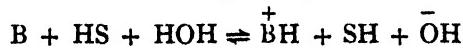


<sup>18</sup> Lowry and Faulkner, *J. Chem. Soc.*, 1925, 127, 2884.

<sup>19</sup> Lowry, *J. Chem. Soc.*, 1927.

<sup>20</sup> *J. Chim. Physique.*, 1928.

In this case the complete catalyst may include either the molecules B and HA, or the ions  $\bar{A}$  and  $\overset{+}{BH}$ , which act as base and acid respectively ; but in aqueous solutions the action will generally be



where the water plays the part of an acid when the catalyst is a base, or of a base when the catalyst is an acid.

I should like to add that, in my opinion, the observation that *a base can only act as a catalyst in presence of an acid*, and conversely, is probably valid in all other cases, if we admit as an obvious exception the occurrence of autocatalysis when the substance catalysed is itself either an acid or a base. This conclusion is supported by the fact that neither acidity nor basicity is possible unless a proton is given by an acid and accepted by a base, since it takes two parties to make an agreement, as well as to make a quarrel.

## PART I. GENERAL RELATIONS.

### HOMOGENEOUS CATALYSIS.

C. N. HINSELWOOD.

*Received 19th July, 1928.*

The most logical way of studying the inner mechanism of catalysis is to begin with the consideration of uncatalysed reactions, and to examine the way in which the phenomena change when catalytic actions are allowed to influence them. This at once raises the question as to which phenomena are appropriately described as catalytic; and in this connection it is very necessary to avoid inconclusive discussions about terminology. There are certain phenomena which all chemists would call catalytic, and others which they definitely would not, but there is a large class about which they would not agree. It would be unfortunate to let the study of the facts themselves suffer because there is not quite general agreement as to whether a given label should be attached. Thus in a discussion of the rôle of catalytic effects in homogeneous reactions a very exact demarcation of catalytic from non-catalytic phenomena would serve no useful purpose.

#### **Homogeneous Reaction Mechanisms.**

It will be convenient to begin by enumerating the principal reaction mechanisms where *prima facie* no catalytic influences enter.

As is well known, the slowness of many chemical reactions, the high temperature coefficient of almost all, and particularly the quantitative relation between temperature and velocity constant prove that in general molecules do not react unless they possess an excess of energy known as the energy of activation.<sup>1</sup>

The simplest kind of homogeneous reaction is probably the bimolecular reaction in a gas, where it seems likely that nothing more is required for chemical change than an impact of sufficient violence between two molecules,<sup>2</sup> either or both of which are forthwith transformed. The evidence for this consists in an agreement between the observed and calculated rates of a number of reactions, but still more in the coherent relationships between the absolute rates of different reactions and the independently determined energies of activation.<sup>3</sup>

Termolecular reactions in gases have interesting peculiarities. Simultaneous collision of three molecules is a rare event: thus, for a termolecular reaction to attain the same rate as a bimolecular reaction at the same temperature it must have a correspondingly smaller energy of activation.

<sup>1</sup> Arrhenius, *Z. physikal. Chem.*, 1889, 4, 226.

<sup>2</sup> W. C. McC. Lewis, *J. Chem. Soc.*, 1918, 113, 471; C. N. Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," 1926; Christiansen, *Proc. Camb. Phil. Soc.*, 1926, 23, 438.

<sup>3</sup> Compare reference 2.

This is found experimentally to be true.<sup>4</sup> Termolecular collisions become less frequent as the temperature increases, with the result that, if the energy of activation is very small, as it may be in a reaction proceeding at the ordinary temperature, the temperature coefficient may actually be negative.<sup>5</sup>

The last type of gaseous reaction is the unimolecular reaction. Unimolecular reactions, are not, strictly speaking, transformations of isolated molecules, as the name suggests. The most satisfactory theory of the mechanism is as follows: the molecule must first have received the energy of activation in a collision with another molecule; if it passes through a suitable internal phase before the next collision it will react, but otherwise it will probably lose the energy again. There is on the average a time-lag between activation and transformation, which can easily be shown to be an essential condition for the reaction to satisfy the experimental criterion of a unimolecular reaction.<sup>6</sup> This time-lag is *a priori* more likely to exist with molecules of complex structure than with simple ones. And there is, in fact, a very marked correlation between the structure of the molecule and the kinetic character of its reaction.<sup>7</sup>

Another important correlation exists: to account for the rate of reaction of complex molecules the Maxwell-Boltzmann law for the distribution of energy must be applied in the form appropriate to many degrees of freedom. In fact, in the decomposition of certain organic compounds, 4 to 6 internal vibrations must be assumed to participate in the activation process.<sup>8</sup> On the other hand, in simple bimolecular reactions only the kinetic energy of the impact need be taken into account.

The distinction between unimolecular and bimolecular reactions is tending to become one of degree only, and indeed the decomposition of ozone shows many signs of being of an intermediate character. It is predominantly bimolecular,<sup>9</sup> but several degrees of freedom are involved,<sup>10</sup> and there is evidence that the activated molecules may be deactivated again.<sup>11</sup>

The study of photochemical changes has afforded much valuable information about reaction mechanisms in general.<sup>12</sup> Molecules which have taken up a light quantum are raised thereby to a high energy level: what follows may be a change in the isolated molecule, or a reaction by a collision between the activated molecule and a normal molecule, or deactivation by collision with a molecule of some foreign substance.<sup>13</sup> In photochemical, and also in purely thermal changes, a mechanism called a chain reaction may come into operation, whereby the energy liberated in the chemical transformation together with the original energy of activation is handed on directly to activate fresh molecules which would not otherwise have been in a state to react.<sup>14</sup>

Passing now to the consideration of reactions in solution, it is probably fair to say that the most remarkable fact about these is the enormous

<sup>4</sup> *J. Chem. Soc.*, 1926, 129, 730.

<sup>5</sup> Bodenstein, *Z. physikal. Chem.*, 1922, 100, 98.

<sup>6</sup> Lindemann, *Trans. Faraday Soc.*, 1922, 17, 598.

<sup>7</sup> *Proc. Roy. Soc.*, 1927 [A], 114, 84.

<sup>8</sup> *Ibid.*, 1926 [A], 113, 230; 1927 [A], 114, 84; 115, 215; Fowler and Rideal, *ibid.*, 1927 [A], 113, 570.

<sup>9</sup> Wulf and Tolman, *J. Amer. Chem. Soc.*, 1927, 49, 1650.

<sup>10</sup> Belton, Griffith and McKeown, *J. Chem. Soc.*, 1926, 3153.

<sup>11</sup> Compare reference 10.

<sup>12</sup> Compare General Discussion on Photochemical Reactions, October, 1925.

<sup>13</sup> Bodenstein, *Trans. Faraday Soc.*, 1926, 21, 525.

<sup>14</sup> Christiansen and Kramers, *Z. physikal. Chem.*, 1923, 104, 451; Bäckström, *J. Amer. Chem. Soc.*, 1927, 49, 1460.

influence of the solvent. This may cause the velocity to vary over a range of a thousandfold, which shows that there is a very intimate association between the solvent and the reacting substances. It is interesting to note, however, that the decomposition of nitrogen pentoxide takes place at the same rate in carbon tetrachloride solution as in the gas,<sup>15</sup> and that the racemisation of pinene is equally fast in the gaseous state, in the pure liquid state and in solution.<sup>16</sup>

Bimolecular reactions in solutions are much slower than in the gaseous state,<sup>17</sup> indicating that the solvent molecules exert a deactivating influence. The effectiveness of bimolecular collisions between molecules with appropriate energies appears to be several powers of ten smaller in the presence of the solvent.

The appearance of ionic phenomena in solution gives rise to a completely new class of reactions. At one time, as we know, there was a tendency to suggest that all reactions were ionic: but this has proved to be definitely untrue. In gaseous reactions, as in innumerable others, ionisation is non-existent or, if present at all, quite secondary.<sup>18</sup>

Homogenous reactions in solids are barely known. Chemical change usually takes place at the surface of the solid and from nuclei of a new phase, where we have a combination of a chemical change and a crystal growth phenomenon.<sup>19</sup>

### Catalytic Actions of Small Traces of Foreign Substances.

The kind of influence which is catalytic in the most clear-cut way is that of a small trace of some foreign compound which causes an increase in the rate of change of the principal substance or substances. Many reactions have been found to involve the intervention of some impurity in the system, not at first imagined to be playing any part in the change. This led to the view that pure substances are in general very unreactive, and that velocity measurements have no absolute significance, because the reaction mechanism is quite different from what it appears to be, and involves the participation of accidental impurities. Among such impurities water, of course, occupies the most prominent position.

This is a convenient place for summarising the objections to such a view.

(i) In the first place it is really a false induction from a number of examples, which are quite different in kind from the homogeneous reactions which are believed to be uncatalysed. Consulting a list of eighty-seven papers in which experiments, with positive or negative results, on the influence of moisture on chemical change are described or discussed, I find that, of the examples where inhibition by drying was reported, the vast majority were interactions between substances in two different phases, where the great influence of an adsorbed film in poisoning or promoting the activity of a boundary surface, or of nuclei, can very well be understood. Of the remainder, a number which might, at first sight, appear homogeneous were really "wall-reactions," such as the union of olefines and halogens, where the "polar" nature of the surface is known to determine the adsorption.<sup>20</sup> Retardation of these reactions by drying is a very interesting and

<sup>15</sup> Lueck, *Z. physikal. Chem.*, 1922, **44**, 757.

<sup>16</sup> D. F. Smith, *ibid.*, 1927, **49**, 43.

<sup>17</sup> Christiansen, *ibid.*, 1924, **113**, 35; Norrish and Smith, *J. Chem. Soc.*, 1928, **129**.

<sup>18</sup> Cf. *Annual Reports (Chem. Soc.)*, 1927, p. 315.

<sup>19</sup> See, for example, Hume and Topley, *Proc. Roy. Soc.*, 1928 [A], **120**, 211.

<sup>20</sup> Norrish, *J. Chem. Soc.*, 1923, **123**, 3006.

important fact, but not one upon which generalisations about homogeneous reactions should be based. If we find that wet or impure iron at the room temperature rusts by an electrolytic process, while dry iron in the nature of the case does not, this says nothing about what will happen with dry oxygen and pure iron heated to some suitable high temperature. Apart from the photochemical union of chlorine and hydrogen, the only reaction in the list, on which normal velocity measurements have been made, and which is believed to be homogeneous, is the combination of nitric oxide and oxygen. This, although stated to be catalysed by water, is equally definitely stated to proceed quite well in the absence of water.<sup>21</sup>

The whole question, however, is perhaps better left for the discussion than treated by an enumeration and *critique* of specific instances.

(2) Many homogeneous reactions, such as the decomposition of nitrogen pentoxide, proceed at constant and reproducible rates.<sup>22</sup> The contrast between these and others where the influence of adventitious impurities controls the rate is most marked.

(3) The relation between the calculated and observed rates of reaction, and particularly the general coherence of the results obtained with homogeneous reactions, makes it probable that we have at least an approximately correct idea of their mechanism, without introducing further hypotheses.

(4) If reactions such as the decomposition of  $2\text{HI}$  or of  $\text{N}_2\text{O}_5$  were determined by collisions of two molecules of  $\text{HI}$  in the first, or a molecule of  $\text{N}_2\text{O}_5$  in the second, with a molecule of an impurity, the order of reaction would have to be one higher than that observed, when determined by a variation in the total pressure.

I do not wish to make dogmatic generalisations about this subject, or to deny that the presence of polar molecules may often have a great effect. But two things will perhaps receive general assent. First, it is important that results obtained in connection with reactions of one kinetic type should not be extended arbitrarily to reactions of another type: in short, a clear theoretical background is necessary in all such investigations. Secondly, the statement that water is always necessary can never be directly disproved, especially if coupled with the proposition that certain substances are undrivable. If we cannot prove that chemical reactions, which apparently take place quite well in the absence of water or other impurity, do not demand the presence of undetectable traces, then what have we to say of the large class of reactions which proceed at reproducible rates and which appear to behave in accordance with simple, self-consistent theories? We can say at least that the reproducibility and consistency ensures that the work done upon them is not being wasted, because even if it be found that another factor has to be introduced, this will involve an addition to existing results as a whole rather than detailed reconstruction. But I do not wish to conceal my own belief that at the moment there is no adequate reason for considering this addition to be necessary.

Examples in homogeneous gaseous reactions of straightforward catalytic mechanisms such as the following



are not common. The classical example, the indirect burning of carbon monoxide by way of the water-gas reaction,<sup>23</sup> is a clear example of the type,

<sup>21</sup> Baker, *J. Chem. Soc.*, 1894, 611; Briner, *J. Chim. physique*, 1926, 23, 848.

<sup>22</sup> Annual Reports, 1927, p. 319.

<sup>23</sup> Dixon, *Phil. Trans.*, 1884, 175, 617.

but can only be observed conveniently in flames. We have recently made an attempt to study the slow combination at temperatures below the ignition point, but surface actions so complicate the matter that no successful isolation of the gas reaction has yet been achieved.

Professor H. B. Dixon<sup>24</sup> observed that the presence of a little nitrogen peroxide lowers the ignition temperature of hydrogen in air by as much as 200° C. He suggested that it would be interesting to investigate the effect on the slow homogeneous combination. It seemed, at first sight, as though this would be a clear case of catalysis by alternate oxidation and reduction of NO, but, as described in the paper which follows, it proved to be quite different. The hydrogen-oxygen combination in the gas phase is a chain reaction. The nitrogen peroxide acts as a kind of detonator, which either initiates the chains sufficiently violently to cause immediate inflammation, or it has hardly any effect at all. There is no concentration at which it provokes a normal more or less rapid reaction.

Many phenomena which look like the operation of homogeneous catalysis are really nothing of the kind. The characteristic reactions of atomic hydrogen only appear in the presence of water vapour, which might seem to show that water catalysed the formation. Wood,<sup>25</sup> however, has definitely shown that the action of the water is to "poison" the walls of the discharge tube, which otherwise cause an immediate catalytic recombination of the atoms. Similar imitation of catalytic effects is found with active nitrogen, where the presence of electronegative impurities appears to catalyse the formation, but in reality stabilises the active product in a quite indirect way.<sup>26</sup>

In solutions, of course, innumerable examples of homogeneous catalysis are known, among which a large proportion are due to ions, the hydron being almost unique in this respect.

### Influence of Solvents and of Inert Gases.

The great influence of solvents, long known, has already been referred to. In contrast with this, foreign gases do not in general have any marked influence on homogeneous gas reactions—though there are some remarkable exceptions to this statement. It has also been mentioned that bimolecular reactions in solution proceed more slowly than would be expected from the heat of activation; this fact indicates deactivation by the collisions with solvent molecules. Molecules in liquids are so close together that the whole environment of a given molecule is quite different from what it would be in the gaseous state; and, indeed, the highly specific nature of solvent influences seems to show that in the liquid state the energy of activation itself must be considerably changed as a result of the quite different forces to which the molecules are subjected. Calculation of effects of this kind is at present beyond our powers.

Ionic reactions in solution are the more dependent on the ionic environment of the reacting molecules as ionic forces act at greater distances than molecular forces. The so-called neutral salt actions are elegantly accounted for by Brönsted's well-known theory, which is to be dealt with in another part of this Discussion.

With those gaseous reactions which are subject to an influence of foreign gases, the effect is to be traced less to a general modification of the environment by the inert gas, and thus of the forces acting on the reacting

<sup>24</sup> Private communication.

<sup>25</sup> Bonhoeffer and Kaminsky, *Z. physikal. Chem.*, 1927, 127, 385.

<sup>26</sup> Proc. Roy. Soc., 1922 [A], 102, 1.

molecules and altering the energy of activation, than to phenomena depending upon a specific transfer of energy from molecules of one kind to those of another.

These phenomena may conveniently be dealt with in a special section.

### Energy Transfer Phenomena.

In order that reaction may occur, the energy of activation must be communicated to the reacting molecules, and, in general, by collision. A reaction depending upon a collision mechanism can only be unimolecular, if the rate at which the statistical equilibrium can be restored, when activated molecules are removed by chemical change, is great compared with the actual rate of reaction. At low pressures, therefore, the rates of certain unimolecular reactions fall away.<sup>27</sup> Hydrogen has a remarkable specific influence<sup>28</sup> in maintaining the velocity constant at its normal value, which it must do merely by maintaining the statistical equilibrium for the energy in the internal degrees of freedom of the other molecules. Helium and nitrogen do not have this effect to anything like the same extent, if at all. Hydrogen does not have any effect on unimolecular reactions in the region where their constants possess the normal value.<sup>29</sup>

In Herzfeld's theory<sup>30</sup> of the union of free atoms to form molecules, ternary collisions of the two atoms with a molecule of a foreign gas are supposed to be necessary, not to communicate, but to remove energy, and so to stabilise the "hot" molecule, which could not otherwise continue to exist. Experimental evidence on this "Dreierstoss" theory is conflicting, both with the union of  $2\text{Br}$  to  $\text{Br}_2$ ,<sup>31</sup> and with the supposed union of nitrogen atoms which may play a part in the decay of active nitrogen.<sup>32</sup>

Energy transfers between molecules are very specific. The specific deactivating influence of oxygen in the photochemical combination of chlorine and hydrogen<sup>33</sup> is one of the best-known examples of this.

A somewhat different kind of phenomena is encountered in the photochemical decomposition of ozone sensitised by chlorine, where each quantum of light originally absorbed by the chlorine causes the decomposition of an ozone molecule, whatever the relative concentrations of ozone and chlorine may be.<sup>34</sup> Thus the activated chlorine must survive a great many collisions without losing its energy, until it finds an appropriate ozone molecule.

Indeed, the transfer of energy in a so-called "Stoss zweiter Art" is something rather analogous to a chemical act.

Collisions of activated molecules with molecules of inert gases are, consistently with this view, often elastic. In the gas reaction between hydrogen and oxygen the reaction chains would be expected to be broken if inelastic collisions with molecules of other gases occur, but lengthened if elastic collisions take place, since the path traversed before the reaction chain reaches the wall of the vessel would be longer in the presence of an inert gas than in its absence. Actually, inert gases, such as argon, helium, nitrogen, and steam, cause a pronounced acceleration of the reaction, indicating

<sup>27</sup> Hinshelwood and Thompson, *Proc. Roy. Soc.*, 1926 [A], 113, 221; Ramsperger, *J. Amer. Chem. Soc.*, 1927, 49, 912, 1495.

<sup>28</sup> Hinshelwood and Askey, *Proc. Roy. Soc.*, 1927 [A], 115, 215.

<sup>29</sup> Busse and Daniels, *J. Amer. Chem. Soc.*, 1927, 49, 1257.

<sup>30</sup> *Z. Physik*, 1922, 8, 132.

<sup>31</sup> Bodenstein, *Sitzungsber. Preuss. Akad. Wiss.*, 1926, 13, 104.

<sup>32</sup> Compare 26.

<sup>33</sup> Chapman and Macmahon, *J. Chem. Soc.*, 1909, 95, 959.

<sup>34</sup> Weigert and Nicolai, *Z. physikal. Chem.*, 1928, 131, 267.

a lengthening of the chains.<sup>35</sup> Thus it must be supposed that the collisions are largely elastic.

In flames, the presence of substances which decrease the rate of emission of radiation and thus cause the retention of energy in the system may be effective in increasing the rate of reaction.<sup>36</sup>

In specific molecular actions a particularly marked influence of like molecules upon one another is often observed, and may be a phenomenon of fundamental theoretical importance. It is encountered in various ways in spectroscopy, in the extinction of the polarisation of mercury resonance radiation with increasing vapour pressure,<sup>37</sup> in the damping of fluorescence in concentrated solutions,<sup>38</sup> and in various chemical reactions. As an example of the latter the decomposition of acetaldehyde in the gaseous state may be quoted.<sup>39</sup> This is a bimolecular reaction, decomposition depending upon a collision between two aldehyde molecules. Collisions with hydrogen, or with nitrogen molecules also provoke decomposition, but they are very much less effective than the collisions between the like molecules.

The newer theories of the atom based upon the wave mechanics do indeed allow a kind of resonance phenomenon, in which there is a marked coupling of two atoms, which may be marked at distances considerably greater than the ordinary molecular diameter.

(Communicated at the meeting): I would like to go one step further in making explicit a point arising from my report. Professor Lowry referred in his introduction, and I referred in my paper to the controversy between those who regard uncatalysed homogeneous reactions as possible, and those who regard the presence of water as essential. In my paper I gave reasons for believing that the latter position is untenable in any general way, but I should like now to suggest a possible synthesis of the views of the two schools which would be acceptable to both.

In the last year we have virtually discovered, or at any rate investigated quantitatively for the first time, a kinetically new kind of chemical change, where there is no region of transition between very slow reaction and explosively rapid reaction. Such changes, which must be exothermic, depend upon reaction chains, which "get out of hand" when a certain critical concentration is exceeded. As examples we have Semenoff's demonstration of a critical pressure above which the combination of phosphorus and oxygen is explosive and below which it is negligible: we have also the reaction between hydrogen and oxygen in presence of nitrous fumes. Semenoff, following Christiansen and Kramers, has worked out very beautifully the theory of such reactions.

Now this distinction between controllable and uncontrollable reactions is kinetically a very fundamental one.

I should like to suggest that, apart from reactions between substances in two phases, of which other explanations are possible, it is in many of these exothermic chain reactions with uncontrollable velocities that moisture plays its famous part. (Semenoff himself refers to Baker's observations on the difficulty of combustion of dried phosphorus.) The moisture may well be concerned in some exothermic process initiating a chain: and the very

<sup>35</sup> Gibson and Hinshelwood, *Proc. Roy. Soc.*, 1928 [A], 119, 591.

<sup>36</sup> Garner and Johnson, *Phil. Mag.*, 1927 [vii], 3, 97.

<sup>37</sup> von Keussler, *Ann. Physik*, 1927, [iv], 82, 793.

<sup>38</sup> *Compt. Rend.*, 1927, 184, 1097.

<sup>39</sup> *Proc. Roy. Soc.*, 1927, [A], 116, 163.

puzzling feature of the "all or nothingness" of the drying effect in such examples as the dissociation of ammonium chloride would be explained.

On the other hand perhaps with the distinction between "controllable" and "uncontrollable" reactions clearly recognised, some of the adherents of the "moisture" school, will be able to concede that the coherent results which can be obtained in investigations of homogeneous reactions with definite velocities are in general—subject naturally to mistakes about individual examples—valid.

If this reconciliation could be effected I think from the point of view of chemical kinetics the Cambridge meeting would have achieved a useful end.

## THE INFLUENCE OF NITROGEN PEROXIDE ON THE UNION OF HYDROGEN AND OXYGEN.—A PROBLEM OF "TRACE CATALYSIS."

By C. H. GIBSON AND C. N. HINSHELWOOD.

(Received 14th June, 1928.)

In connection with some recent investigations on the rate of combination of hydrogen and oxygen, Professor H. B. Dixon communicated to us his observation that traces of nitrogen peroxide have a remarkable influence on the burning of hydrogen in air, lowering the ignition temperature by as much as 200° C. He suggested that it would be interesting for us to examine the effect on the slow, isothermal combination.

The obvious hypothesis to make seemed to be that nitrogen peroxide accelerates the reaction between hydrogen and oxygen by playing the part of an oxygen carrier, being alternately reduced and oxidised. Since few, if any, examples of this kind of homogeneous catalysis in gaseous systems have been quantitatively investigated, we were very ready to follow up Professor Dixon's suggestion.

The results have been rather unexpected; and, indeed, lead to some general conclusions about the nature of "trace catalysis" which are not without interest.

There is a certain slow reaction, which may very well involve the alternate reduction and oxidation of nitrogen peroxide, *i.e.*, a true catalytic reaction, but, as long as the amount of nitrogen peroxide is small, this reaction is of no importance, and is not the one concerned in the phenomenon of ignition.

At about 400° C., nearly 200° below the ordinary explosion temperature, hydrogen and oxygen alone combine very slowly indeed, and on the surface of the vessel only. A sufficiently small trace of nitrogen peroxide produces no observable effect: as the amount is increased, a sharply defined limit is reached beyond which almost immediate explosion of the hydrogen and oxygen occurs when the gases are admitted to the reaction vessel. With still greater amounts of nitrogen peroxide a second limit is reached, as sharply defined as the first, beyond which explosion no longer occurs, but only the very slow reaction already referred to.

The important fact is that both these limits are quite sharp: there is no region of rapid but measurable reaction, transitional between the region of non-reaction and the region of explosion.

This proves that the explosion is not the culmination of a catalysed combination of oxygen and hydrogen : if it were, there would be a region of nitrogen peroxide concentration where the speed of combination became comparable with that of the normal reaction at higher temperatures. The explosion must be initiated by ordinary ignition of the hydrogen and oxygen by the heat liberated in some independent reaction of the nitrogen peroxide.

The rate of liberation of heat in any volume element of the gas by this independent reaction will either be greater than the rate at which it can be conducted away, or it will be less. If it is greater, there will be ignition of the hydrogen and oxygen : if it is less, there will be no appreciable effect. Thus the sharp limit between the regions of explosion and of non-reaction is explained. The independent reaction of the nitrogen peroxide is analogous to a detonator which either works completely or fails altogether.

The existence of the limit at higher, as well as at lower, nitrogen peroxide concentrations means that the rate of the "detonator" reaction falls off at higher concentrations, or that the nitrogen peroxide itself dissipates the heat in some way. This itself requires to be explained, but the details of the special explanation do not in the least affect what has been said.

If the rapid, heat-producing reaction were one between nitrogen peroxide and some other gas, e.g. hydrogen, adsorbed on the walls of the vessel, then, with increasing concentration of nitrogen peroxide, the rate of reaction could first increase and then decrease again as the surface became saturated. This is a well-known type of heterogeneous reaction. The mechanism is only mentioned here as an illustration of a possible one : it is not necessarily the true one.

What is really important is that we have here an example of a reaction, apparently so strongly catalysed by a foreign substance that a mere trace lowers the explosion temperature  $200^{\circ}\text{C}$ . The analogy between this and the action of traces of moisture on the ammonium chloride dissociation is obvious. With nitrogen peroxide quantitative experiments are easy, whereas they are nearly impossible with water. Nobody has ever been able to measure the rate of dissociation of ammonium chloride, or to ascertain whether there is a sharp or a continuous change, on drying, between reaction and non-reaction. Experiments now show that, at least with nitrogen peroxide and the hydrogen-oxygen combination, the transition is sharp : the phenomenon therefore, is, properly speaking, hardly a catalytic one, but a thermal one.

If nitrogen peroxide were a common impurity in gases, and if the effect on the ignition point of hydrogen and oxygen were known, without the additional facts that have just been stated, the question might easily be raised, whether the measurable combination which can be studied between  $530^{\circ}$  and  $580^{\circ}\text{C}$ . did not really depend upon traces of nitrogen peroxide. In the light of what has been said, however, it will be seen that the answer to this question is a definite negative. The possibility that examples, such as that of water and ammonium chloride, are analogous should at least be borne in mind by those who question the existence of uncatalysed homogeneous reactions.

The method of experiment was the same as that used in the previous investigation of the rate of combination of oxygen and hydrogen.<sup>1</sup> Porcelain reaction vessels were employed, the course of the reaction being followed by observations of the rate of pressure change.

Traces of nitrogen peroxide of known amount were introduced into the reaction mixture in the following way : Three gas-holders were attached to

<sup>1</sup> Roy. Soc. Proc., A, 118, 170 (1928).

the reaction vessel, one containing pure oxygen, one pure hydrogen, and one a mixture of hydrogen with a known amount (1-2 per cent.) of pure nitric oxide. By varying the relative proportions of gas admitted to the vessel from the two latter, the total hydrogen being kept constant, the nitrogen peroxide concentration of the resulting mixture could be adjusted to any desired value. Oxygen was always admitted last.

The following results were obtained at 371° C. in an unpacked porcelain bulb of about 200 c.c. capacity, the pressure of hydrogen being 400 mm. in each experiment and that of oxygen 200 mm. :—

Amount of NO added. (mm.)	Result of Experiment.	Amount of NO added. (mm.)	Result of Experiment.
0·15	No appreciable reaction	0·20	Exploded
0·17	" " "	(0·22	No appreciable reaction)
0·17	" Exploded)" "	0·22	Exploded
(0·17		0·23	"
0·18	No appreciable reaction	0·28	"
0·18	" " "	0·30	"
0·18		0·43	"
		0·61	"
		0·63	"
		0·70	"
		0·80	"

Amount of NO added. (mm.)	Result of Experiment.
0·83*	Rate less than 1 per cent. per minute
0·83*	" Exploded)" " "
(0·85	Rate less than 1 per cent. per minute
0·90*	" " " "
1·10*	" " " "
1·36*	" " " "
1·60*	" " " "

In the experiments marked \* there was no question of the mixture having combined very rapidly but without audible explosion: this was clearly shown by the fact that on evacuation of the reaction vessel after the experiment a bright flash occurred when the concentration was reduced so as to pass through the "explosive" region once more.

Similar series of experiments were made at other temperatures:—

Temperature.	Pressure of NO (mm.).	
	Lower Limit of Explosion.	Upper Limit of Explosion.
371° C.	0·18	0·83
390° C.	0·18	1·45
404° C.	—	2·35
421° C.	0·19	>3·3

These results are plotted in the figure, from which it is evident that the upper and lower limits should meet somewhere between 340° and 360° C. At this point there should be only one mixture which explodes. An indirect confirmation of the general correctness of this conclusion was afforded by a

series of experiments carried out at  $352^{\circ}\text{C}$ . No actual explosion occurred,

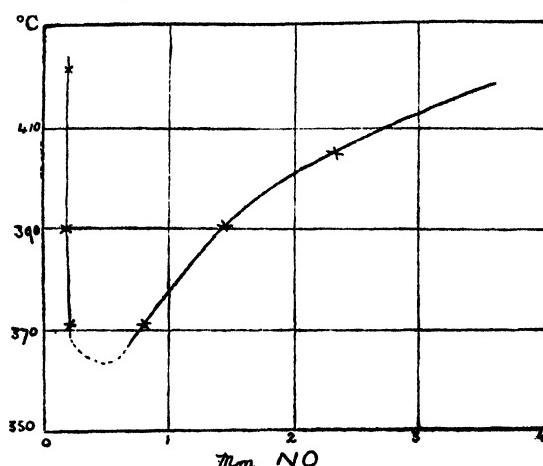


FIG. I.

but there seemed to be a distinct line of demarcation, at  $0.5\text{ mm.}$ , between mixtures which flashed on evacuation and those which did not. It seems reasonable to suppose that, though the conditions of concentration are greatly changed before the flash occurs, the separating line gives the concentration at which explosion would just have occurred at a slightly higher temperature. This gives,

therefore, a rough idea of where the minimum in the curve occurs.

Mm. NO . . . . .	0·17 0·27 0·33 0·42 0·50 0·51 0·60 0·70 0·80 0·87
Flash (+) or no flash (-) on evacuation . . . . .	- - - - + - + + + +

A few experiments were also made in a bulb packed with fragments of broken porcelain. At  $371^{\circ}\text{C}$ . no explosion occurred at any concentration. At  $421^{\circ}\text{C}$ . the lower limit of explosion was at approximately the same concentration as in the unpacked bulb, while the upper was between  $3\cdot6$  and  $6\cdot6\text{ mm. NO}$ .

## CATALYTIC PHENOMENA IN THE TAUTOMERISM OF CERTAIN $\alpha$ -DIKETONES.

By HENRI MOUREU.

(Received 6th July, 1928, and translated from the French.)

The  $\alpha$ -diketones in certain cases show the phenomena of tautomerism with the greatest clearness, although the tautomerism of these compounds has for a long time been disregarded. Thus, methylbenzylglyoxal and phenylbenzylglyoxal are both known in two distinct and pure tautomeric forms.

	Melting Point.	Colour.
Methylbenzylglyoxal $\text{C}_6\text{H}_5-\text{CH}_2-\text{CO}-\text{CO}-\text{CH}_3$	{ Form A ( $69^{\circ}-70^{\circ}\text{ C.}$ ) <sup>1</sup> Form B ( $17^{\circ}-18^{\circ}\text{ C.}$ ) <sup>2</sup>	Colourless Lemon yellow
Phenylbenzylglyoxal $\text{C}_6\text{H}_5-\text{CH}_2-\text{CO}-\text{CO}-\text{C}_6\text{H}_5$	{ Form A ( $90^{\circ}\text{ C.}$ ) <sup>3</sup> Form B ( $35^{\circ}-36^{\circ}\text{ C.}$ ) <sup>4</sup>	Yellowy-white Lemon yellow

<sup>1</sup> C. Dufraisse and H. Moureu, *Bull. Soc. Chim.*, 4, 41, 1607 (1927).

<sup>2</sup> H. Moureu, *Comptes Rendus*, 186, 380 (1928).

<sup>3</sup> C. Dufraisse and H. Moureu, *loc. cit.*; O. Widman, *Ber.*, 49, 484 (1916); H. Jorlander, *Ber.*, 50, 406 (1917); Malkin and Robinson, *J. Chem. Soc.*, 127, 369 (1925).

<sup>4</sup> H. Moureu (*Unpublished Results*).

For the sake of simplicity the form with the higher melting-point is called form A and that with the lower melting-point form B.

Chemical studies<sup>5</sup> have shown that the isomerism of the A and B forms of these  $\alpha$ -diketones is of the keto-enolic type: the A forms seem to consist of one of the possible stereoisomers of the keto-enolic form  $R-\text{CH}:\text{C}(\text{OH})-\text{CO}-\text{R}'$ , whilst the B forms seem to be the true diketone  $R-\text{CH}_2-\text{CO}-\text{CO}-\text{R}'$ . The tautomerism of these compounds from the benzils  $\text{Ar}-\text{CO}-\text{CO}-\text{Ar}$  which cannot give enolic forms (see specially Schönberg and his co-workers).

*The Activity of Alkaline Catalysts.*—When one of the B-isomers in a super-cooled state is treated with a trace of alkaline catalyst, such as an organic amine, there follows a change, more or less rapid according to the nature and concentration of the catalyst, from form B into form A.

If the temperature is below that at which equilibrium exists between forms A and B in a saturated solution of the isomer A in isomer B, isomer A crystallises out and the transformation of isomer B into isomer A proceeds gradually to completion. Thus, at room temperatures the transformation always takes place in this direction. As a first approximation the transformation is unimolecular. The following table gives an idea of the comparative activity at ordinary temperature of the catalysts used:—

Approx. Period of the Change. (Phenylbenzylglyoxal).	Concentration.	Catalyst.	Concentration.	Approx. Period of the Change. (Methylbenzylglyoxal).
—	—	Benzylamine	1/200	3 days
—	—	Diethylaniline	1/200	7 hours
1 hour	1/200	Quinoline	1/200	2 hours
20 minutes	1/200	Pyridine	1/200	45 minutes
—	—	Diethylamine	1/250	A few seconds
A few seconds	1/200	Piperidine	1/250	"
—	—	Potash	1/1000	12 minutes

On the other hand, when the catalyst reacts on form A at the boiling-point of form B, a complete change takes place from A to B since B is the more volatile form.<sup>6</sup>

Finally, at all temperatures intermediate between those at which one or other of the isomers separates from the mixture by crystallisation or distillation, a state of equilibrium varying with the temperature exists between forms A and B.

*The Catalytic Action of Glass.*—Special mention is now made of the action, which is perhaps too often neglected, of ordinary glass. Glass is an active catalyst, particularly at high temperatures, for the changes of the A and B forms. Thus a sample of the B isomer of methylbenzylglyoxal left in a super-cooled state at room temperature in a glass tube (sealed in order to avoid the effect of air) is changed completely in a few weeks into the A isomer. The rapidity of the change increases considerably with temperature, and at 100° C. more than 40 per cent. of the material has undergone change in less than an hour. This activity of glass is yet more pronounced in the case of phenylbenzylglyoxal, of which the A form is changed completely into the B form by simple distillation *in vacuo*. These changes are completely suspended if quartz is used instead of ordinary glass.

<sup>5</sup> See especially H. Moureu, *Comptes rendus*, 186, 503 (1928).

<sup>6</sup> If the catalyst is volatile (amines) an inverse change takes place in B after distillation, and the product finally obtained is the initial A isomer. This inverse change is avoided by using as catalyst a trace of fixed alkali such as sodium carbonate.

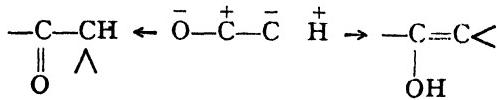
These facts point to the conclusion that the transformations, which at first sight appeared to be spontaneous, or to be due solely to the action of heat, are in reality always *catalysed*, the glass being in this case the catalyst.

*The Equilibrium A  $\rightleftharpoons$  B.*—If one of the preceding isomers is heated in the presence of an appropriate catalyst at a temperature at which neither crystallisation nor distillation of one of the forms takes place, a rapid change occurs in the index of refraction, until an index is reached which is fixed and quite definite for the temperature in question. For a given  $\alpha$ -diketone the final values (at a given equilibrium temperature) are very nearly the same, whether one starts from the A or the B isomer.

Thus, for methylbenzylglyoxal, the index of refraction of the mixture in equilibrium at 100° C.<sup>7</sup> is  $n_{16^{\circ}3}^D = 1.5879$ , using isomer A as starting point, and  $n_{16^{\circ}3}^D = 1.5883$  when B is used. The index of refraction of the pure B isomer is  $n_{16^{\circ}3}^D = 1.5192$  (observed) and that of the A isomer (calculated) is  $n_{16^{\circ}3}^D = 1.627$ . The composition of the mixture in equilibrium at 100° C.<sup>7</sup> calculated from these indices is 64 per cent. of A and 36 per cent. of B. It varies with temperature, and at 70° C., for example, the equilibrium mixture contains about 71 per cent. of A isomer and 29 per cent. of B. Analogous results have been obtained for phenylbenzylglyoxal: from the variation in the equilibrium constant the heat of the reaction A  $\rightleftharpoons$  B has been calculated (with the assistance of Van't Hoff's equation) for each  $\alpha$ -diketone studied. The conclusions drawn from this study of the catalysed equilibrium in a homogeneous medium in the case of these  $\alpha$ -diketones are as follows:—

- (1) Increase of temperature favours the ketonic form (B).
- (2) The change from the ketonic form (B) to the enolic form (A) takes place with evolution of heat.

*The Mechanism of Catalytic Actions.*—In the solid state the A and B forms do not show any tendency to change and the changes which have been observed can only, it seems, be produced in the liquid state or in solution. In the crystalline state these molecules then seem incapable of reaction and it is only in the homogeneous phase that these can exist, the "normal" form (Thorpe and Ingold), or the active molecule possessing "mesohydric" linkages (Oddo), or mono-electronic "semi-valencies" (J. Perrin), of which Lowry<sup>8</sup> gives a suggestive representation in the multipolar ion



How, then, does the catalyst act? Does it act simply in the process of activation or is its action manifested in the orientation which it tends to give to the activated molecule?

An attempt closely to synthesise the mode of action of the catalyst in changes of this type, which takes completely into account certain characteristics of the phenomenon, has just been carried out by Lowry<sup>9</sup> in an electrolytic theory of catalysis by acids and bases. It may be asked, however, whether the "intermediate compounds" do not themselves, also, play

<sup>7</sup> The mixture is heated for some minutes at 100° C., in the presence of one part of piperidine in five hundred, which is then neutralised by a trace of oxalic acid; after cooling rapidly the index of refraction of the super-cooled mixture is taken.

<sup>8</sup> T. M. Lowry, *Bull. Soc. Chim.*, 4, 35, 917 (1924).

<sup>9</sup> T. M. Lowry, *J. Chem. Soc.*, 2554 (1927).

a part in these catalytic changes, and an example in confirmation of this hypothesis is given.

The enolic (A) forms of  $\alpha$ -diketones interact with antimony trichloride to form crystalline salts,<sup>1</sup> the observed chemical properties of which can be satisfactorily represented by the formula R—CH=C(OSb Cl<sub>2</sub>)—CO—R'.

The diketonic (B) forms of these same  $\alpha$ -diketones lead to the same salts, although the reaction is slower. But if these salts are decomposed in the cold with a very mild reagent such as hydrogen sulphide or tartaric acid, *only the enolic (A) form* is recovered. The passage from B to A is therefore effected by the formation of an intermediate compound, the antimony salt, although in this case catalytic action does not take place, since the antimony salt is stable in the conditions of the experiment. It is possible to imagine that other analogous salts might be less stable than that of antimony and might even not be capable of isolation; they would not the less play the rôle of an intermediary necessary in the change from B to A. Thus in the case, for example, of the alkalis we have, on the one hand, the undoubted formation of salts (as indicated by the solubility of the two isomers in dilute alkalis and by an abundant evolution of hydrogen when either isomer is treated with metallic sodium—Dufraisse and Moureu<sup>1</sup>), and, on the other hand, no less incontestable catalytic action. One can, furthermore, conceive an analogous compound (easily dissociable and consequently too ephemeral to be capable of isolation except under experimental conditions which might be difficult to realise in practice) between amines and the before-mentioned tautomeric forms.

In the transformations which have been considered here, the intermediate formation of a compound between the catalyst and the product therefore appears to be inevitable. The question still unanswered, for which the experiments herein cited do not provide a solution, is to know whether this union is an essential phase of catalysis, that is, whether it is a condition of which the suppression will stop the catalysis itself, or whether on the contrary it only represents an accessory phenomenon, unconnected with the real mechanism of the transformation.

## IONISATION IN CHEMICAL CHANGE.

By N. R. DHAR.

*Received 23rd July, 1928.*

In publications from these laboratories<sup>1</sup> the importance of the generation of ions and electrons in exothermal chemical reactions has been emphasised. Apart from the well-known researches of Richardson and co-workers<sup>2</sup> the results obtained by Haber and Just,<sup>3</sup> Pinkus,<sup>4</sup> Bloch,<sup>5</sup> Tanatar and Burkser,<sup>6</sup> Potter,<sup>7</sup> Brewer<sup>8</sup> and others show definitely that ionisation takes place in all the exothermal reactions investigated by the above workers.

Moreover, we have obtained evidence of the generation of ions in the

<sup>1</sup> *J. physical Chem.*, **28**, 948 (1924); *Z. anorg. Chem.*, **141**, 1 (1924); **144**, 307 (1924); **159**, 103 (1926).

<sup>2</sup> *Phil. Trans.*, A, **222**, 1 (1921); *Proc. Roy. Soc.*, A, **115**, 20 (1927).

<sup>3</sup> *Ann. Physik* [4], **36**, 308 (1911).

<sup>4</sup> *Compt. rend.*, **150**, 694 (1910).

<sup>5</sup> *Proc. Roy. Soc., B*, **91**, 465 (1915).

<sup>6</sup> *J. Chim. Physique*, **18**, 366, 412 (1920).

<sup>7</sup> *J. Russ. Phys. Chem. Soc.*, **45**, 1 (1913).

<sup>8</sup> *J. Amer. Chem. Soc.*, **46**, 1403 (1924).

slow oxidation of sodium and of sodium sulphite in air. Recently Finch and Stimson<sup>9</sup> have shown that when mixtures of gases like hydrogen and oxygen, carbon monoxide and oxygen are adsorbed on the surfaces of gold and silver the metal surfaces become charged. It seems likely that ionisation takes place during the process of adsorption which is possibly chemical in nature. Although in a recent communication Hinshelwood<sup>10</sup> has concluded that chemical change is not necessarily accompanied by anything more than small ionisation of the secondary or accidental character, we are of the opinion that ionisation is of common occurrence in exothermal chemical changes. If proper precautions are taken and the ionisation is measured before a good deal of recombination occurs we are likely to get evidence of ionisation in most exothermal chemical changes.

We shall now briefly state how many types of changes can be explained from the point of view of generation of ions in exothermal chemical changes, the ions and electrons thus generated being absorbed by the reacting substances which are activated.

### 1. Induced Reactions.

We<sup>11</sup> have shown that though mercurous chloride is not formed by boiling mercuric chloride and oxalic acid in the dark, the addition of a drop of potassium permanganate leads to the formation of mercurous chloride. It is evident that the exothermic reaction between oxalic acid and potassium permanganate induces the reaction between oxalic acid and mercuric chloride. The exothermic reaction between potassium permanganate and oxalic acid possibly generates ions and electrons which could be absorbed by oxalic acid molecules which would be activated and lead to the reduction of mercuric chloride. Numerous cases of induced reactions have been studied by us as well as by other investigators, and in almost all cases the primary reaction is exothermic, and the primary reactions are likely to generate ions and electrons which are the activators.

### 2. Influence of Moisture in Chemical Reactions.

It is well known that many chemical changes are accelerated by the presence of moisture or a substance with a high dielectric constant. Loeb,<sup>12</sup> Tyndall and Grindley,<sup>13</sup> Hasse<sup>14</sup> and others have shown that the mobility of gaseous ions is greatly decreased in presence of water vapour or HCl, and it is believed that a cluster consisting of moisture or HCl with the gaseous ions is formed. Baker and others have shown that anhydrous sodium and chlorine do not ordinarily react, but in presence of moisture the reaction takes place vigorously. It is likely that in absence of moisture the few ions that are generated as the product of the chemical change between sodium and chlorine recombine or escape from the arena of the change, because of the high mobility of the gaseous ions. If, on the other hand, moisture is introduced, cluster formation with moisture, ions and gaseous chlorine molecules takes place. The clusters move slowly and hence there is greater chance of the chemical change between sodium and chlorine.

<sup>9</sup> Proc. Roy. Soc., A, 116, 379 (1927).

<sup>10</sup> Annual Reports Chem. Soc., 24, 314 (1927).

<sup>11</sup> J. Chem. Soc., 111, 664 (1917).

<sup>12</sup> Proc. Nat. Acad. Sciences, 12, 35, 42 (1926).

<sup>13</sup> Proc. Roy. Soc., A, 110, 341, 358 (1926).

<sup>14</sup> Phil. Mag. 7 series, 1, 139 (1926).

### 3. Chemiluminescence and After-glow of Gases.

In presence of  $\text{CH}_4$ ,  $\text{H}_2\text{S}$ , etc., the after-glow of active nitrogen is accelerated. In presence of a substance with a high dielectric constant because of cluster formation the chance of activation of the gases of the reacting substances is greatly improved. The reversion of the active substances to an inactive form leads to chemiluminescence. Consequently, after-glow or chemiluminescence would be more easily visible in presence of substances with high dielectric constants.

In a foregoing paper<sup>15</sup> we have shown that adsorption of gases by solid catalysts is possibly chemical change and that ions and electrons are produced in the process of adsorption, and these act as activators.

### 4. Abnormal Photochemical Yield.

It is well known that the photochemical decomposition of  $\text{H}_2\text{O}_2$  and combination of  $\text{H}_2$  and  $\text{Cl}_2$  are highly exothermic changes, and that Einstein's law of photochemical equivalence is not applicable to these cases. Many molecules decompose or combine per quantum absorbed. We have advanced the view that ionisation takes place when these substances decompose or react on illumination and the ions generated are absorbed by the inactive molecules which are now activated even in absence of light, and consequently the amount of chemical change is greater than the amount of light absorbed.

The ionisation potential of gases such as hydrogen, oxygen, etc., being high, it would be very difficult to ionise them thermally. Consequently the ionisation observed in the explosion of hydrogen and oxygen, carbon monoxide and oxygen, acetylene and oxygen, and methane and oxygen appears to be mainly chemical.<sup>16</sup>

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<sup>15</sup> *Z. anorg. Chem.*, **159**, 103 (1926).

<sup>16</sup> Compare Garner and Saunders, *Trans. Faraday Soc.*, **22**, 342 (1926); Saunders and Kato, *ibid.*, **23**, 248 (1927); and Saunders, *ibid.*, **23**, 256 (1927).

## NEGATIVE CATALYSIS IN SLOW AND INDUCED OXIDATIONS.

By N. R. DHAR.

*Received 23rd July, 1928.*

It is well known that a solution of sodium arsenite is not oxidised by atmospheric oxygen under ordinary conditions. On the other hand, a solution of sodium sulphite is readily oxidised to sodium sulphate by air. Now if we mix together a solution of sodium arsenite and sodium sulphite and expose the mixture to air, both the oxidations take place simultaneously. At the same time a curious phenomenon takes place. The velocity of the oxidation of sodium sulphite becomes very small in presence of sodium arsenite, i.e. sodium arsenite which is undergoing a slow oxidation acts as a powerful negative catalyst in the oxidation of sodium sulphite.

In previous papers<sup>1</sup> we have shown that manganous salts act as powerful negative catalysts in the oxidations of formic and phosphorous acids by chromic acid, and manganous salts can easily pass into the manganic state. Moreover, it has been shown by myself and other workers that various organic substances, notably hydroquinone, brucine, etc., act as negative catalysts in the oxidation of sodium sulphite by air and that all these organic substances are themselves readily oxidised. It is well known that the oxidation of phosphorus by oxygen is retarded by vapours of various organic substances like ether, alcohol, and turpentine, and the oxidation of chloroform is retarded by the presence of a small quantity of alcohol. Now all these negative catalysts are good reducing agents. Hence we came to the conclusion in a publication in 1921 that the phenomenon of negative catalysis is observable when the catalyst is likely to be readily oxidised.<sup>2</sup>

Since the publication of the foregoing results and conclusions several workers have paid attention to the problem of negative catalysis. In a series of very interesting researches Moureu and Dufraisse<sup>3</sup> have studied the absorption of oxygen by benzaldehyde, acrolein, acetaldehyde, turpentine, etc., in presence of phenol, thymol and numerous other substances.

It is practically impossible to explain satisfactorily from a single point of view all the diverse experimental results obtained by Moureu and his co-workers; but one thing is certain that the majority of the substances investigated which act as negative catalysts are good reducing agents. Similarly the researches of Lifschitz and Kalberer<sup>4</sup> have shown that ether retards the slow oxidation of magnesium alkyl halides, and Delépine<sup>5</sup> has shown that some reducing agents can act as negative catalysts in the oxidation of several organic sulphur compounds by air. Consequently the experimental work available on negative catalysis has amply verified the accuracy of our statement that negative catalysis is possible when the catalyst is liable to be readily oxidised.

We have shown<sup>6</sup> that the velocity of the decomposition of nitrous acid according to the equation :—



is greatly retarded in presence of glucose, maltose, cane sugar, glycerol, etc. The decomposition of nitrous acid is a case of auto-oxidation and reduction taking place simultaneously. Consequently reducing agents like cane sugar, glucose, maltose, etc., act as negative catalysts in this reaction involving auto-oxidation and reduction.

Recently we have studied<sup>7</sup> the induced oxidation of sugars, starch potassium stearate, palmitate, oleate, uric acid and other nitrogenous, substances by passing air at the ordinary temperature, in presence of reducing agents like ferrous hydroxide, cerous hydroxide, and sodium sulphite. In all these cases we have observed that the velocity of the oxidation of ferrous hydroxide, cerous hydroxide and sodium sulphite is greatly retarded by the presence of carbohydrates, fats and nitrogenous substances. The maximum retardation is produced by carbohydrates, and then come fats, and finally nitrogenous substances. Moreover, we have shown that the induced

<sup>1</sup> *J. Chem. Soc.*, 111, 707 (1917); *Annales de chim.*, [ix], 11, 130 (1919).

<sup>2</sup> *Proc. K. Acad. Wetensch. Amsterdam*, 20, 1023 (1921).

<sup>3</sup> *Compt. rend.*, 174, 258 (1922); 175, 127 (1922); 176, 624, 797 (1923), and subsequent publications.

<sup>4</sup> *Z. physik. Chem.*, 102, 393 (1922).

<sup>5</sup> *Compt. rend.*, 174, 1291 (1922).

<sup>6</sup> *Z. Elektrochem.*, 31, 255 (1925).

<sup>7</sup> *J. physical Chem.*, 29, 799 (1925); 30, 939 (1926).

oxidation of sugar is markedly retarded by fats and the oxidation of fats is retarded by carbohydrates. The oxidation of nitrogenous substances is remarkably retarded by either fat or carbohydrate. The protein sparing quality of carbohydrates and fats has been observed by early workers on metabolism. We have proved that carbohydrates, fats and nitrogenous substances can be oxidised by passing air at the ordinary temperatures in presence of sunlight or artificial light. The presence of fat markedly retards the photochemical oxidation of carbohydrates, and *vice versa*. These researches have thrown considerable light on the problem of metabolism in diabetes.

As practical applications of the principles involved in negative catalysis, we have been able to preserve large quantities of oils, turpentine, sodium sulphite, etc., from being oxidised by air by adding to them traces of hydroquinone. Ordinary India rubber can keep without being hardened when coated with a thin layer of turpentine or alcoholic solution of hydroquinone. Moreover, paper and wood in tropical countries can be preserved from being brittle by a coat of these reducing agents. In tropical countries all substances like paper, rubber, wood, etc., are being subjected to constant photo-oxidation by atmospheric air due to the presence of sun and diffused daylight and this process can be markedly retarded by coating them with reducing agents such as turpentine, hydroquinone, etc.

In recent papers<sup>8</sup> we have advanced an explanation of induced oxidation based on the generation of ions in exothermic reactions. It is well known that ions are generated in the oxidation of phosphorus, sodium, etc. It is likely that these ions can activate molecules of oxygen which thus become reactive and induce chemical changes which are not possible with molecular oxygen. In the spontaneous oxidation of sodium sulphite by air we have obtained evidence of ionisation. These ions will activate the molecules of oxygen which will react on sodium arsenite. As the activated molecules of oxygen contain an excess of energy, they would readily combine with substances like sodium arsenite, oxalic acid, etc., which normally are not oxidised by molecular oxygen at the ordinary temperature. We know that sodium sulphite readily combines with molecular oxygen, but activated molecules of oxygen would hardly differentiate between molecules of sodium sulphite and arsenite because of their increased energy contents. Consequently, an activated molecule of oxygen would be practically as good an oxidising agent towards sodium arsenite as towards sodium sulphite.

Recently Jorissen and co-workers<sup>9</sup> have discussed some cases of induced reactions and activation of oxygen. They have observed that in presence of sodium sulphite, sodium antimonite can be oxidised by atmospheric oxygen. As far as I know I was the first to observe the phenomenon of negative catalysis in induced reactions. What Jorissen, Engler and Wild and others did was to find out whether Schönbein's law is applicable to oxidation reactions or not. These authors were not concerned with the velocity of the oxidation reactions and did not observe the phenomenon of negative catalysis in induced reactions.

We have come to the conclusion<sup>10</sup> that in many cases the negative catalyst, like sulphur, hydroquinone, etc., which markedly retards the oxidation of benzaldehyde, sodium sulphite, etc., is actually oxidised. Moreover, in many cases, the negative catalyst forms additive or adsorption compounds with one of the reacting substances, especially reducing agents such as

<sup>8</sup> *J. physical Chem.*, **28**, 948 (1924); *Z. anorg. Chem.*, **141** (1924), **1**, 144, 307 (1924).

<sup>9</sup> *Rec. Trav. Chim.*, **42**, 855 (1923); **43**, 582 (1924).

<sup>10</sup> *Z. anorg. Chem.*, **144**, 289 (1925).

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sodium sulphite, benzaldehyde, acrolein, turpentine, etc., and the complex is oxidised as a whole. We have come to the conclusion that in many cases the phenomena of negative catalysis, induced oxidation and complex formation are essentially connected.

Since a chemical reaction has finite velocity it is generally assumed that all the molecules of the reacting substances are not in the same state of activation. Moreover, chemical changes are supposed to take place between active molecules. Hence, normally, the active molecules of the reducing agents combine with the active molecules of oxygen and form an unstable peroxide. Now if another reducing agent is introduced into the system, the active molecules of oxygen tend to combine with the molecules of the second reducing agent. Moreover, the active molecules of the two reducing agents may combine to form an adsorption or additive compound. Consequently the presence of the second reducing agent is likely to lead to the decrease of the oxidation of the first reducing agent. This is the probable mechanism of negative catalysis in slow oxidation reactions.

Recently<sup>11</sup> we have shown that the glow obtained by passing ozonised oxygen through solutions of dyes like eosin, neutral red, uranine, methylene blue, etc., is markedly retarded on the addition of substances like nicotine, hydroquinone, sodium sulphite, turpentine, etc.

It is well known that oxygen is a negative catalyst in the photochemical combination of hydrogen and chlorine and in other halogenation reactions. It is quite possible that in all these cases the oxygen actually combines with the reducing agents under the influence of light and hence can act as a negative catalyst. Similarly the retarding influence of oxygen in the decomposition of solutions of organic ferric salts and tetrabenzoylethylene is due to the combination of the oxygen with the reducing agents under the influence of light.

Christiansen<sup>12</sup> has introduced the conception of chain reaction in explaining negative catalysis. Recently Bäckström<sup>13</sup> has obtained abnormally high quantum yield in the photochemical oxidation of benzaldehyde, heptaldehyde and sodium sulphite solutions. The photochemical reactions are markedly subject to the action of the same inhibitors which retard the dark reactions. These results are supposed to prove that chain reactions take place in the photochemical as well as thermal chemical changes. In publications from these laboratories<sup>14</sup> we have shown that the abnormal quantum yield in exothermal photochemical changes can be satisfactorily explained from the point of view of the generation of ions without the assumption of chain reactions. In the thermal oxidation reactions the negative catalysts retard the chemical changes by actually taking up oxygen and being oxidised themselves. Consequently the two reducing agents compete for the oxygen and thus the velocity of the main reaction is lowered. Hence the conception of the occurrence of chain reactions in thermal oxidations seems unnecessary.

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<sup>11</sup> *Z. anorg. Chem.*, **173**, 125, 1928.

<sup>12</sup> *J. physical Chem.*, **28**, 145 (1924).

<sup>13</sup> *J. Amer. Chem. Soc.*, **49**, 1460 (1927); *Medd. K. Vetens-Kapsakad. Nobel Inst.*, **1927**, 6, Numbers 15 and 16.

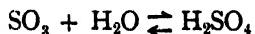
<sup>14</sup> *Z. anorg. Chem.*, **159**, 103 (1926); *Z. physik. Chem.*, **120**, 75 (1926).

# INHIBITION IN CHEMICAL REACTIONS.

By ERIC K. RIDEAL.

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In a number of cases the retardation effected by the addition of an inhibiting agent is directly proportional to the inverse concentration of the inhibitor; such is the case for the inhibiting effect of water in the decomposition of oxalic acid by sulphuric acid<sup>1</sup> and of hydrobromic acid on the hydrolytic decomposition of bromosuccinic acid.<sup>2</sup> This strict relationship is obtained in cases where the reduction in concentration of a reacting constituent is effected on addition of an inhibitor. In the former case sulphuric anhydride appears as a catalytic reactant, its concentration being determined by the relationship



and in the latter a strongly catalytic anion is replaced by a more weakly active acid.

Another large group of inhibited reactions includes those in which a catalyst is present in but small quantities, e.g. cupric ions in the oxidation of sulphites.<sup>3</sup> Such a catalyst can be removed by effecting chemical combination, e.g. with cyanide. We again obtain a simple relationship between reaction velocity and inhibitor concentration from the equations

$$(1) v = kRC.$$
$$(2) C + I \rightleftharpoons CI \quad (C)(I) = K(CI).$$
$$(3) v = \frac{kRK(CI)}{I}.$$

The interest in inhibition of chemical reactions is at the present time to a great extent focussed in those reactions which under certain conditions can readily attain high velocities, such as oxidation, halogenation and processes of polymerisation. Before an adequate interpretation of inhibition phenomena in these fields can be obtained we require further information on these reactions especially in the transition stages from slow to rapid velocities. Semenoff<sup>4</sup> makes a convenient division of such reactions into two types. In the first the adiabatic exothermic reaction is sufficient to accelerate the reaction by ordinary kinetic excitation to the explosion point, in the second group, reaction centres are formed which act as foci of reaction. It appears that whilst a number of autoxidation processes may conform to the first type a great number must be included in the second category.

A number of views have been expressed as to the mechanism of reaction in this group. Primarily the atom chain mechanism of Nernst,<sup>5</sup> employed for the hydrogen chlorine combination, has been adapted, notably by Bodenstein and Berthoud<sup>6</sup> for the halogenations. We may note

<sup>1</sup> Müller, *Z. physik. Chem.*, **41**, 483, 1902.

<sup>2</sup> Bredig and Lichtz, *Z. Elektrochem.*, **12**, 459, 1906.

<sup>3</sup> Titoff, *Z. physik. Chem.*, **45**, 641, 1903.

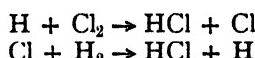
<sup>4</sup> *Z. Physik*, **57**, **48**, 1928.

<sup>5</sup> *Z. Photochemie*, Doin et Cie, Paris, 1927.

<sup>6</sup> *Z. Elektrochem.*, **24**, 335, 1918.

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that reaction chains in hydrogen chlorine mixtures can be initiated by hydrogen atoms as shown by Marshall and by the interaction of alkali metals and the halogen by Polanyi. The inhibition of such atom chains can readily be effected by the addition of atom acceptors or catalysts effecting the recombination of atoms. Whilst the atom chain mechanism gives a clear picture of the high quantum yield in the case of, say, hydrogen-chlorine mixtures it does not in itself give any reason for the progressive increase in velocity when a critical speed is reached, for unless some link in the chain can start a new one the velocity can only rise by purely thermal means. Some additional assumption must be made that in addition to the actual chain reaction, e.g.—



a further reaction of the type  $\text{H}'\text{Cl} + \text{Cl}_2 \rightarrow \text{HCl} + z\text{Cl}$  can be effected. Inhibition can then be effected by deactivation of the excited molecule of hydrochloric acid. Whilst an adequate interpretation of the hydrogen bromine reaction is given by the atomic hypothesis, the many differences, e.g. in the inhibiting effect of oxygen between this reaction and in, say, the reaction between cyclohexane and bromine<sup>7</sup> lead one to doubt whether the atom mechanism offers a completely satisfactory explanation.

A second type of chain mechanism for reactions in which the phenomenon of inhibition is most marked, is that advanced by Christiansen,<sup>8</sup> in which it is assumed that the freshly formed energy rich products excite a reactant molecule either by collision or by emission and absorption of radiation. We may note that the decomposition of hydrogen peroxide is frequently considered to be a chain reaction of this type. The decomposition of this substance is readily inhibited by substances as varied as barbituric acid, phenacetin and sodium pyrophosphate. That a surface decomposition is in many cases a cause of instability has been shown by Gurwicz.<sup>9</sup> Wright and I have found that on a variety of surfaces the rate of decomposition is at a maximum at the isoelectric point of the surface when the adsorption of non-electrolytes is at a maximum. There appears little doubt that inhibitors do poison the surface in this reaction. The other reactions for which the chain mechanism of Christiansen has been advanced are the oxidation of substances such as benzaldehyde, investigated in detail by a number of workers including Backstrom,<sup>10</sup> Reiff,<sup>11</sup> and Brunner,<sup>12</sup> as well as oxidation of numerous substances including hydrocarbons in which the phenomenon of inhibition has been studied so brilliantly and exhaustively by Moureu and his co-workers including Dufraisse. In photochemical oxidation of benzaldehyde the fact that more than one molecule of benzaldehyde, per quantum absorbed, undergoes oxidation is well established. In addition it would appear that in the thermal oxidation of benzaldehyde the phenomenon of an induction period is noted, in other words, if the chain mechanism be correct some link in this chain must be capable of initiating fresh chains. Since many inhibitors undergo oxidation during the process of inhibition it is frequently assumed that the oxygen is the

<sup>7</sup> Wood and Rideal, *J. Chem. Soc.*, 2466, 330, 1927.

<sup>8</sup> *J. physical Chem.*, 104, 459, 1923.

<sup>9</sup> *Z. physik. Chem.*, 107, 1923; Rice, *J. physical Chem.*, 31, 1352, 1927, and Williams, *Trans. Farad. Soc.*, 24, 245, 1928.

<sup>10</sup> *J. Amer. Chem. Soc.*, 49, 140, 1927.

<sup>11</sup> *Ibid.*, 48, 2893, 1926.

<sup>12</sup> *Helv. Chim. Act.*, 10, 707, 1928.

reactant excited by collision or radiation and not the material undergoing autoxidation. This view can be stated in terms of the following equations :—

- (1)  $A + O_2 + h\nu \rightarrow AO'_2$ .
- (2)  $AO'_2 + O_2 \rightarrow AO_2 + O'_2$ .
- (3)  $A + O'_2 \rightarrow AO'_2$ .

Such a mechanism does not permit of a rising velocity under iso-thermal conditions ; to account for this two modifications have been suggested, one by Semenoff in the oxidation of phosphorus—



the other, in which it is assumed that the peroxide formed in the primary chain can of itself initiate chains thus—

- (1)  $A + O_2 + h\nu \rightarrow AO'_2$ .
- (2)  $AO'_2 + O_2 \rightarrow AO_2 + O'_2$ .
- (3)  $A + O'_2 \rightarrow AO'_2$ .
- (4)  $AO_2 + A \rightarrow AO' + AO$ .
- (5)  $AO' + O_2 \rightarrow AO + O'_2$ .

These two mechanisms thus provide for an increase in reaction centres or points from which chain propagation is possible, as the reaction proceeds. Inhibitors would operate either by deactivation of the excited product  $AO'_2$  or in undergoing oxidation, they merely break the chains. There is no doubt that in these oxidations the catalytic effect of the walls is not negligible factors at low temperature. Likewise the facts that dry chlorine and sodium and, similarly, dry phosphorus or benzaldehyde and oxygen do not react with one another, as well as the experiments of Baker, lead one to suspect that the reaction centres of Semenoff are not identical either with atoms or reactant or intermediary unstable or stable products as visualised in the hypothesis of Christiansen. The rate of generation of these novel reaction centres or chain initiators would then govern the rate of initiation of chains and thus the reaction velocity. An isothermal reaction with a period of induction would involve a chain system which initiated other chains either by the formation of new reaction centres of the same or different type as the original. The extraordinary efficiency of inhibitors in these reactions would thus be readily intelligible in that they destroy or prevent the formation of the reaction centres which are responsible for chain propagation, *i.e.* are chain initiators, and *do not act primarily* by deactivating or combining with an excited product, although such reactions can occur when once a chain has been initiated. These reaction centres or chain initiators are formed most readily on wet walls and, in gases containing moisture, we note also that they are likewise destroyed by surfaces. The early experiments of Thompson and of Thomas on the hydrogen oxygen combinations, of Briner on nitric oxide synthesis as well as those of Haber, Brewer and Finch on oxidation processes, and of Kunsmann on the synthesis of ammonia lead to the view that in some cases at any rate, those chain initiators may well consist of ions. Dhar apparently subscribes to the view that the reaction centres consist in all cases of ions. Even in more complex cases such as the lowering of the ignition point of hydrogen oxygen mixtures by nitrogen peroxide and the increase in luminescence of active nitrogen by oxygen, those substances possessing strong electron affinities may operate by forming ions, leaving the positive ion as a reaction centre. On increasing the quantities of these substances, deactivation of

some link in the reaction chain occurs and the "catalytic" effect of these substances is lost.

It is worth while at this stage to enquire as to the manner by which charged gaseous ions can actually facilitate chemical combination. Hitherto we have assumed that they act as reaction centres for initiating a chain. It is assumed that during chemical action at the walls at low temperature or in the gas phase at higher temperature, a few ions are formed, these on recombination provide sufficient energy to start off a reaction chain. Another possibility exists when ions are generated in gases in that clusters can be formed and these clusters undergo reaction. The experiments of Lind<sup>13</sup> and Mund<sup>14</sup> on reactions producing  $\alpha$  particles indicate quite clearly the formation of reaction chains or clusters around each ion going into reaction. It can readily be shown<sup>15</sup> that in reacting gases the composition of the cluster will depend on the relative deformabilities of the two reacting constituents. A maximum effective chain length of some twelve molecules is the highest to be anticipated in the reaction of a cluster. It is, however, probable that in some cases (e.g. hydrogen and oxygen, or hydrogen and chlorine), on the explosion of a cluster a few fresh ions may be formed, giving the necessary continuous increase in concentration demanded by the increasing velocities.

An interesting application of the cluster hypothesis is to be found in the reduction of copper oxide by hydrogen. If atomic hydrogen be utilised the copper oxide is smoothly reduced and for every hydrogen atom hitting the copper but one enters into reaction. If now the atom be converted into the  $H^+$  ion it is found that three atoms of hydrogen disappear; in other words, in reactions of the stable cluster  $H_3^+$  formed from  $H + H_2$  and one readily noted in discharge tubes the whole enters into reaction; the effective chain length in the reduction of copper oxide is in this case three.

It will be observed that no unanimity of view has as yet been expressed as to how an ion can facilitate chemical action. The ion may serve merely as a reservoir of energy in so far that the energy set free on neutralisation sets off the surrounding cluster or initiates a chain. Alternatively we may imagine that round the ion the reactants are held by electrostatic attraction and, under the influence of the field, undergo distortion and reaction without neutralisation of the ion, which in this case is acting simply in a catalytic capacity, its life as a catalyst being finished when neutralisation is effected either in the gas phase or at surfaces.

<sup>13</sup> *J. physical Chem.*, 10, 580, 1912.

<sup>14</sup> Solvay Report, 1928.

<sup>15</sup> Rideal, *ibid*, 1928.

## PHOSPHORESCENCE AND AUTOCATALYSIS DURING SLOW COMBUSTION.\*

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One of the first manifestations of chemical change in many combustible gaseous mixtures on heating is a faint luminous glow or phosphorescence

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which, unlike a true flame, does not possess sharp boundaries but extends in the form of a cloud throughout the heated gas mixture. This phosphorescence was observed by Sir Humphry Davy with ether vapour in the neighbourhood of a hot platinum wire and later, in 1882, by Sir William Perkin,<sup>1</sup> with the vapour of organic substances at the surface of a copper sphere. Carbon bisulphide vapour phosphoresces at a low temperature and it has been studied in detail by Professor H. B. Dixon,<sup>2</sup> especially with regard to the extinguishing action of ethylene, coal gas, etc., on the glow. There is an interesting comparison between the extinction of phosphorescence by inhibitors and the action of lead tetra-ethyl in raising the self-ignition temperature of gaseous mixtures whilst in both cases there is an initial suppression of chemical change, indicating the similarity of the mechanism of inhibition. A similar comparison was pointed out a century ago by Thomas Graham<sup>3</sup> between the suppression of the glow of phosphorus and of the inflammability of hydrogen and oxygen mixtures by the presence of certain vapours such as that of ether or turpentine oil.

Recent researches on the problem of detonation in the internal combustion engine have revealed that the "knocking" characteristics of a fuel are closely associated with the formation of highly unstable but reactive organic peroxides at the surface of nuclear particles during the period of slow combustion, and the action of lead tetraethyl in delaying detonation is apparently to inhibit the formation of these primarily formed addition products of fuel and oxygen molecules, moloxides or primary peroxides.<sup>4</sup> The presence of "active" oxygen, presumably in the form of peroxides, has been shown in the products of slow combustion of hydrogen, coal gas, methane, ethylene, ether, petrol, hexane, etc., but the addition of the vapour of "anti-knockers" diminishes or stops the formation of "active" oxygen.

Autoxidation of benzene to phenol occurs when benzene vapour is admitted to a hexane-air mixture undergoing slow combustion, indicating the formation of organic peroxides from hexane.<sup>5</sup> Similarly, benzene and alcohol vapour, methane, etc., which inhibit phosphorescence are oxidised at relatively low temperatures when added to carbon bisulphide undergoing incipient oxidation in air, suggesting that the primary oxidation product of carbon bisulphide is also an active peroxide which is reduced by the inhibiting substances. This removal of the primary highly reactive peroxides, which catalyse the combustion, accounts at once for the powerful action of mere traces of certain substances in suppressing phosphorescence, raising the self-ignition temperature, delaying detonation and suppressing chemical change. An important feature of inhibitory action is the provision of nuclei at the surface of which oxidation begins. Thus, Lord Rayleigh and Professor H. B. Dixon regard inhibitors of phosphorescence as acting by taking prior possession of the nuclei of molecular aggregates, rendering them resistant to oxidation. Similarly, Professor H. L. Callendar in his nuclear theory of detonation regards the nuclei as centres of ignition; and lead tetra-ethyl, by concentration in the drops decomposes the primary peroxides formed at the surface, thus delaying detonation.

<sup>1</sup> *J. Chem. Soc.*, 41, 363.

<sup>2</sup> Dixon and Russell, *J. Chem. Soc.*, 1899, 75, 600; Dixon, *Rec. Trav. Chim.*, 1925, 44, 305.

<sup>3</sup> *Pogg. Ann. Physik*, 1829, 17, 375.

<sup>4</sup> Callendar, *Engineering*, 4th Feb., 1927.

<sup>5</sup> Mardles, *J. Chem. Soc.*, 1928, 872.

### Experimental Methods.

For observing phosphorescent flames and the presence of fog in gaseous mixtures on heating, the apparatus consisted of a combustion tube about 2 feet in length and 1 inch in diameter round the central 8 inches of which was wound an electric heating coil inserted between mica to secure more uniform heating and protection from draughts. The tube was provided at one end with a glass end plate and a side tube through which the fuel vapour mixtures entered, whilst projecting into the tube from the other end was a thermocouple. Air was supplied to this tube by a pressure drum similar to that described previously,<sup>4</sup> the only addition being that of an adjustable pressure release valve. The air was bubbled through sulphuric acid, passed through tubes containing calcium chloride, soda lime, and cotton wool filters, through a small calibrated orifice (the pressure difference across which was measured by a water manometer) into a special form of wick carburettor where it was charged with the vapour required. The wick had the effect of providing an evaporation surface at constant level, enabling mixture strengths to be maintained constant to the degree of accuracy required. The metals employed for the thermo-couple were platinum and platinum-rhodium; the junction was enclosed in glass in order to avoid the possibility of catalytic action. The couple was calibrated against a platinum resistance thermometer, reading on a Whipple indicator; a Callendar nickel heater being employed for the purpose. For the observations on fog formation, a parallel beam of light was passed down the glass tube and a movable mirror was arranged so that when required the source of illumination (pointolite, arc or quartz mercury vapour lamp) could be changed immediately; and the fogs were viewed by scattered light, in a direction perpendicular to the parallel beam. Observations of the chemical changes were made in glass tubes and bulbs by methods already described,<sup>5</sup> the stream of gases passing through the tubes at approximately the same rate as in the experiments for phosphorescence and fog formation. The glass bulbs of about 200 c.c. capacity, one filled with dry air and the other with the gas mixture under test, were connected differentially to a toluene manometer such as in Callendar's compensated gas thermometer. The increase of pressure due to heating was balanced by the differential arrangement so that the toluene manometer measured the pressure increase due to chemical change.

The mixture strengths referred to in the paper are expressed as percentages of the vapour or gas by weight in air. For sake of convenience the experimental results have been divided into 4 parts, *viz.*: Results with (a) carbon bisulphide, (b) ethyl ether, (c) acetaldehyde and amylene, (d) hexane.

#### (a) Experimental Results with Carbon Bisulphide.

When a carbon bisulphide-air mixture 19 per cent. rich, was passed through the glass tube used for observing fog formation and the temperature slowly raised the first sign of change was the appearance of a few wisps of very fine blue haze just discernible with care below 100° C. As the temperature approached 150°, the fog which had hitherto remained very thin began to increase and a very faint phosphorescence, visible only with special care, appeared. With further increase in temperature the light beam in the fog test became brighter, the phosphorescence became stronger and more extended whilst sulphur dioxide could be detected at about 175°. At 195° there was a strong explosion with a lilac coloured flame, followed by

an intense fog and copious evolution of sulphur dioxide. These combustion changes were followed also by means of the differential bulb apparatus.

The first signs of chemical change were noted about  $100^{\circ}$  C., corresponding to the fog formation, by a small difference in pressure which slowly increased until about  $145^{\circ}$  was reached when acceleration of the changes occurred corresponding to the beginning of luminescence and formation of pronounced fog. It will be seen from Fig. 1 that the changes occur at a lower temperature with the leaner mixture, a behaviour contrary to that observed with ether and hexane, etc., the curves relating the temperature of initial combustion, T.I.C. (*i.e.*, when it is possible first to detect sulphur dioxide, aldehydes, and other oxidation products), with mixture strength being smooth U-shaped curves. The relation between mixture strength and T.I.C. is of some interest, since it is not in accord with the law of mass action. It supports the view that nuclear particles are formed prior to oxidation, these particles, probably ionised, forming the centres of chemical change.

With carbon bisulphide-air mixtures it was found that with the leaner mixtures self-ignition occurred from  $119^{\circ}$  upwards, whilst with the richer mixtures inflammation was delayed and slow combustion with phosphorescence occurred as first described by Turpin, 1890.<sup>6</sup> He stated that a stream of air passing over liquid carbon bisulphide could be sent through a glass tube heated to  $200^{\circ}$  where it glowed without bursting into flame, depositing a red-brown volatile solid on the glass with the formation of sulphur dioxide.

Differences in the character of inflammation were noted, and these appeared to depend on the presence of slow combustion products, because a lower ignition temperature was obtained when the gas mixture was passed suddenly into a hot tube than that found when the tube was gradually heated whilst the gas mixture was passing. This behaviour is in accord with the statement of Dixon<sup>2</sup> that if the gas mixture failed to ignite in his concentric tube the power of inflammation was restored by a prolonged sweeping out of the cylinder, which suggested that some product of combustion remained and inhibited ignition.

The anomalous behaviour of carbon bisulphide-air mixtures in that the richer mixtures appear to be more stable against oxidation, contrary to the general behaviour of hexane, hydrogen, coal-gas, etc., in air, calls for some comment. The excess carbon bisulphide appears to behave

TEMPERATURES OF INITIAL COMBUSTION OF HEXANE, ACETALDEHYDE, ETHYL ETHER AND AMYLENE COMPARED WITH THOSE OF CARBON BISULPHIDE

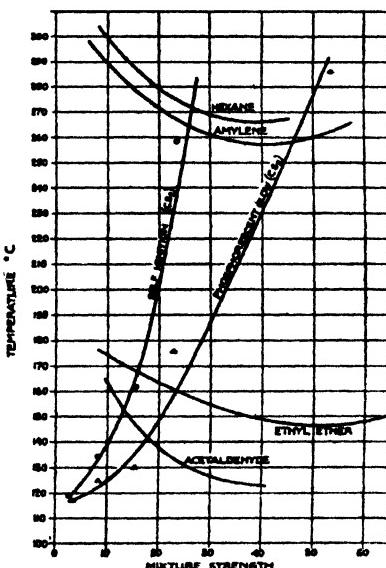


FIG. I.

as its own inhibitor. This would follow quite naturally if there is interaction between a carbon bisulphide molecule and its primarily formed peroxide, for example as in the following equation :—



whereby the catalyst  $\text{CS}_2\text{O}_2$  is removed and combustion suppressed.

A similar behaviour probably occurs to a smaller extent with other gaseous mixtures including carbon monoxide and hydrogen, and this effect must play an important part in the mechanism of combustion and the tendency of a fuel to detonate in the engine.

*Fog and Phosphorescence Experiments with Carbon Bisulphide.*—The fogs extended throughout the whole length of the tube and were blue. This suggested that they were composed chiefly of solid, rather than liquid particles. The method of experiment was to switch out all lights as soon as fog appeared, and to continue heating. Immediately the phosphorescent glow commenced, the temperature was observed, the heating then being continued in darkness until the vapour reached the temperature at which ordinary combustion occurred.

As the temperature increased the glow, at first very faint, became brighter and more extended, until eventually it appeared to divide and a slow moving blue flame or a rapid explosive flame, according to mixture strengths, passed along the tube. The temperature at which this occurred is referred to in the table below as the "ignition temperature," although actually there appears to be continuous transition from the state of phosphorescent combustion to ignition as ordinarily understood.

The glow appeared always at a temperature above that at which fog was first observed ; in the case of weak mixtures only slightly above. Mixture strengths ranging from 4 per cent. to 50 per cent. were employed, and over the range 4 per cent. to 20 per cent. the temperature of fog formation was in the neighbourhood of  $100^\circ\text{C}$ . With the very rich mixture however, this temperature rose to  $240^\circ\text{C}$ . The temperature at which the glow appeared and inflammation occurred, increased with increase of mixture strength, at first slowly, and later quite rapidly ; these observations being in accord with the view that in very rich mixtures, the excess carbon bisulphide acts as its own inhibitor.

TABLE I.—EFFECT OF MIXTURE STRENGTH ON RESULTS WITH CARBON BISULPHIDE.

Mixture Strength (by Weight).	Initial Fog Temp. ( $^\circ\text{C}$ .)	Initial Glow Temp. ( $^\circ\text{C}$ .)	Ignition Temp. ( $^\circ\text{C}$ .)	Nature of Ignition.
4·5	112	119	119	Cool slow moving blue flame.
8·9	124	126	130-140	Faster vivid blue flame ; quiet burning.
16·1	110	130	162	Fast but quiet flame of greater brilliance.
23·0	97	177	259	Brilliant flame ; mildly explosive.
54·0	240	288	355	Less brilliant flame ; less explosive and redder colour.

With the 54 per cent. mixture the inflammation was accompanied by copious deposition of a white solid, presumably white sulphur.

*Action of Inhibitors.*—Using a carbon bisulphide mixture of 4 per cent. which gave a steady glow at  $200^\circ$ , the effect of many substances was investi-

gated. Benzene vapour had a marked effect, no fog, glow or sulphur dioxide being observed until a temperature of  $350^{\circ}$  was reached. Bromine, amyl nitrite and ethyl nitrate behaved similarly to benzene; it was necessary to heat the tube, after removal of the nitrite to a temperature of nearly  $400^{\circ}$  C., before the glow could be induced to reappear, whilst after using ethyl nitrate or bromide, no glow could be obtained until the tube was taken down and cleaned. Iodine was less effective than bromide. Pentane vapour quickly extinguished the glow, as did acetaldehyde, ethyl acetate, ethylene dibromide, and pyridene in order of decreasing efficacy. Acetone and acetic acid both inhibited the glow completely after a few minutes, but did not appear to be very powerful. Chloroform vapour and ammonia reduced the intensity of the glow considerably but did not extinguish it unless added in excess. Methyl and ethyl alcohols suppressed the glow completely. Ethyl ether vapour had the same effect as iron carbonyl; the glow was reduced in intensity, and became less concentrated; after a little time this diffuse glow weakened still further, then began to fluctuate both in position and intensity, and finally passed quickly into separate combustion waves (blue flames) along the tube. With lead tetra-ethyl the glow at  $200^{\circ}$  was extinguished. At  $400^{\circ}$  C., with the same amount of lead tetra-ethyl, the glow became only slightly less intense and more diffuse. Aniline and phenol were found to have little or no effect on the glow at  $200^{\circ}$ . The four gases, acetylene, coal gas, ethylene, and sulphuretted hydrogen, all extinguished the glow completely and with about equal rapidity but the glow reappeared a few minutes after the gas had been shut off. The only substance found whose effect was the reverse of inhibitory was carbon monoxide. The glow was intensified considerably and extended in the presence of this gas. This result being in contradiction to that recorded by Dixon,<sup>2</sup> the experiment was carefully repeated and confirmed. The effect of copper on the glow at  $200^{\circ}$  C. was investigated by inserting a small piece of copper gauze, which almost filled the tube's cross-section. The intensity of the glow appeared to remain unaffected, but it became concentrated on the surface of the gauze.

The following experiments were carried out by the tube method to investigate the action of inhibitors and the presence of metals on the slow combustion of carbon bisulphide-air mixtures. When *iso*-pentane, a powerful inhibitor, was added to a 22 per cent. carbon bisulphide-air mixture the slow combustion of the carbon bisulphide was delayed until the T.I.C. of *iso*-pentane (*viz.*:  $300^{\circ}$ ) was reached. By means of a companion tube through which the same *iso*-pentane mixture alone in air was being passed, it was found that the degree of oxidation of pentane was about the same in both tubes over the temperature range  $300^{\circ}$ - $400^{\circ}$ .

Other organic substances tried in the phosphorescence experiments were used. With all of these the slow combustion was delayed. The self-ignition temperature was also considerably raised. Typical results are given in Table II.

The effect of *iso*-amyl nitrite and ethyl nitrate vapour on the combustion behaviour of a 5 per cent. carbon bisulphide mixture which ignited with some violence at  $159^{\circ}$  was tried. The addition of about an equal amount of *iso*-amyl nitrite raised the self-ignition point to  $245^{\circ}$  which was found to be nearly the same for the *iso*-amyl nitrite mixture when taken alone, *viz.*,  $250^{\circ}$ . Below this temperature there appeared to be very little change, apart from a fog formation, until  $240^{\circ}$  was reached when the litmus solution began to be slowly affected. Ethyl nitrate vapour also delayed the self-ignition temperature and the T.I.C.

TABLE II.—THE SUPPRESSION OF OXIDATION IN CARBON BISULPHIDE-AIR MIXTURES.

Mixture.	Temperature when Litmus Solution was first Affected (° C.).
(a) 22 per cent. bisulphide in air	190 (Ignition at 320).
(b) Mixture <i>a</i> , diluted with 15 per cent. acetylene	237 (No self-ignition though temp. raised to 350).
(c) Mixture <i>a</i> , diluted with 20 per cent. coal gas	400 (No self-ignition though temp. raised to 500).
(d) Mixture <i>a</i> , diluted with 10 per cent. ethylene	380 (No self-ignition though temp. raised to 450).
(e) Mixture <i>a</i> , diluted with 30 per cent. carbon monoxide	310
(f) Mixture <i>a</i> , diluted with 10 per cent. benzene vapour	350
(g) Mixture <i>a</i> , diluted with 7·5 per cent. ethyl alcohol vapour	340
(h) Mixture <i>a</i> , diluted with 15 per cent. ethyl ether vapour	280 (Fog at 180 but no ignition below 450). (Ignition at 350).
(i) Mixture <i>a</i> , diluted with 10 per cent. aniline	

*Action of Lead Tetra-Ethyl, Iron Carbonyl, Metals, etc.*—When a few fragments of iodine were added to the warm tube, the gas mixture apparently remained unchanged even though the temperature was raised to 400°. A 4 per cent. carbon bisulphide mixture in air exploded loudly at 163° but when the air supply was first bubbled through iron carbonyl the first sign of change was at 180° when a fine blue fog appeared, although the presence of sulphur dioxide could not be detected. At 245° there was a yellow flash of light followed by a copious evolution of sulphur dioxide. Repeating the experiment with lead tetra ethyl a similar result was obtained, quiet inflammation occurring at 343°. Some strips of copper gauze were rolled and inserted into the combustion tube—the mixture which exploded at 165° now remained unchanged until 177° was reached when a small amount of sulphur dioxide was evolved. At 375° the mixture ignited. The copper gauze during the experiment had become slightly darker but no marked change had occurred. A number of other metals were tried and the results are shown in Table III. :—

TABLE III.—ACTION OF METALS ON THE OXIDATION OF CS<sub>2</sub> VAPOUR.

Metal.	Temp. when slow Combustion began, noted by Change in Litmus Solution (° C.).	Self-Ignition Temp. (° C.).
None	155	163
Copper gauze . . . . .	177	375
Lead foil . . . . .	180	205
Iron filings sprinkled on bottom of tube . . . . .	180	185
Zinc (granular) . . . . .	280	above 400
Tin . . . . .	about 250	340
Aluminium turnings . . . . .	320	350
Nickel foil . . . . .	200	375
Small piece of platinum foil . . . . .	180	210
Bismuth . . . . .	330	335
Magnesium ribbon . . . . .	270	307

The remarkable extinguishing action of ethylene on the inflammation of carbon bisulphide mixtures was apparently first discovered by Frankland<sup>7</sup> who was investigating the cause of a street coal gas explosion. Later, in 1890, Turpin<sup>8</sup> showed that sulphur dioxide raised the self-ignition temperature from 160° to 260°. Dixon<sup>9</sup> has investigated the action of hydrogen, carbon dioxide, etc., on the self-ignition temperature and phosphorescence, and found that whilst some substances were relatively inert others were noxious or poisonous even in traces. White<sup>8</sup> who investigated the lower limit of combustion of carbon bisulphide mixtures found that it was specifically catalysed by some product of oxidation.

*The Mechanism of Inhibition.*—A number of chemical experiments were undertaken to investigate the possible mechanism of inhibition which would account at once for the inhibition of phosphorescence, of self-ignition and the delaying of the slow combustion observed. When the following substances were vaporised and mixed with air the temperatures of initial oxidation changes were observed to be: coal gas 590°, ethylene 453°, benzene 660°, ethyl alcohol (aldehyde formation) 425°. Although benzene was thus found to be very stable to oxidation by air yet when added to a carbon bisulphide mixture and passed through a hot tube at about 400°, the benzene was oxidised to phenol; the addition of bromine water to the water through which the exit gases had bubbled, precipitated the bromophenols. Similarly when coal gas, ethylene or ethyl alcohol was added to a carbon bisulphide mixture at a temperature below their respective T.I.C.'s and during the slow combustion of the carbon bisulphide autoxidation occurred in all the cases as indicated by the formation of aldehydes. The autoxidation of benzene, coal gas, ethylene, and ethyl alcohol during the slow combustion of carbon bisulphide in air can be accounted for by the formation of a peroxide. This primary peroxide ( $CS_2O_2$ ) is probably the catalyst of combustion and its destruction during the autoxidation of benzene, alcohol, ethylene, etc., accounts at once for the inhibition of chemical change and consequently of phosphorescence and self-ignition.

Dixon attempted to explain the inhibition phenomenon by suggesting that the carbon monosulphide or its molecular aggregation with carbon bisulphide is responsible for phosphorescence. He considered that ethylene and other inhibitory molecules fastened or condensed on the nucleus poisoning it against further oxidation at an early stage. This view of the function of carbon monosulphide has been criticised by White<sup>8</sup> from the results of experiments on the spontaneous ignition of sulphur in the presence of inhibitors.

### Experimental Results with Ethyl Ether.

A highly explosive peroxide has been isolated from the products of slow combustion of ethyl ether by Legler.<sup>9</sup> The formation of reactive peroxides is also indicated by the autoxidation of benzene in the presence of ether undergoing slow combustion in air at a temperature when benzene vapour alone in air remained unoxidised. When pure ether vapour in air was passed through glass tubes which were gradually heated, the T.I.C. was noted by the deposition of dew on the cold sides of the tube at the exit end and by the test for aldehydes. The temperatures given in Table IV. were found with different mixture strengths:—

<sup>7</sup> *Chem. News*, 5, 3, 1862.

<sup>8</sup> *J. Chem. Soc.*, 1927, 793.  
<sup>9</sup> *Ber.*, 1885, 18, 3343.

TABLE IV.

Mixture strength . . . .	8·3	22	28	45	49	55	65
Temp. initial combustion (° C.) . . . .	175	165	159	147	146	145	147

Iron carbonyl was found to influence the combustion of ether in air to a greater extent than lead tetra ethyl, the amount of active oxygen present in the products of slow combustion being reduced to a greater extent by the iron compound. With a mixture of ether in air (8·3 per cent.) which had a T.I.C. of 170°, the effect of iron carbonyl and lead tetra-ethyl was to lower the T.I.C. to 140° and 145° respectively. A similar result was obtained when metals were introduced into the combustion space. Iron turnings had a greater effect than lead foil. Copper and bronze turnings had a marked effect in inhibiting peroxide formation but were less effective than zinc and tin in delaying the formation of carbon dioxide. Magnesium and aluminium caused only slight changes in the combustion.

The quantitative results obtained by chemical analysis of the products of combustion are shown in Table V. The aldehydes were calculated as acetaldehyde: the acids as acetic acid.

TABLE V.—COMBUSTION OF ETHER IN AIR.

Temp. (° C.) . . . .	145	200	320	450
Mixture strength (%) . . . .	35 15 15 *	35 15 15 *	35 15 15 *	35 15 15 *
Aldehydes . . . .	3·7 7·5 1·7	46·5 — 39	37 47 30	22 35 15
Acids . . . .	0·8 1·2 0·2	21 — 12	15·5 22·5 3·7	5 9 1·5
CO <sub>2</sub> . . . .	0·5 1·2 0·5	3·5 — 2·1	10·5 14·5 7·5	29 25 30
CO . . . .	—	—	24 — 16·5	27 — —

*Fog and Phosphorescence.*—On slowly heating an ether vapour-air mixture of strength about 5 per cent., the following changes were observed with regard to fog formation. Between 30° and 50° a very faint wisp of fog appeared which, however, disappeared on slight further heating. At about 180°, a thin fog would again appear in the cooler portions of the experimental tube. In the hotter portion of the tube, the particles were probably too small to be observed. The fogs became more intense on further heating and particle motion was always visible. With light from a pointolite lamp, the fog appeared quite blue in colour at first, when viewed perpendicularly to the beam. As the temperature was increased and the fog became thicker, its colour became whiter. Observed obliquely to the tube, these fogs showed brilliant bands of colour, which repeated themselves in definite orders along the length of the tube. Decided thickening of the fogs occurred near 190° C., and the tube temperature was observed to rise sometimes as much as 15°. At about 220° C. "combustion waves" commenced; these took the form of blue flames visible in a darkened room. On further heating, the flames became more frequent, until finally at about 240° continuous combustion commenced with a steady blue phosphorescent flame. This flame was quite distinct from an ordinary hot flame. With the passing of the first combustion wave the already intense fog thickened, and with each wave a momentary rise in temperature of 10° to 15° occurred.

*Action of Inhibitors.*—The tube temperature was kept at about 250° C. and the mixture strength was 5 per cent. approximately. Benzene had no effect on the glow and lead tetra ethyl caused only a slight diminution in its intensity. Iron carbonyl completely extinguished the glow after causing

\* With iron carbonyl vapour present.

it to pass from the bright flame to the diffuse and weak phosphorescent form. Bromine nearly extinguished the glow, whilst iso amyl nitrite and methyl alcohol both reduced its intensity, but failed to extinguish it completely. Nitrogen peroxide extinguished the glow; a single small "puff" being sufficient for the purpose. When a small amount of nitrogen peroxide was passed continuously into the tube with the ether-air mixture, a fog was obtained at ordinary temperature. This fog persisted up to 500°. No glow was observed: but above 500° a violent explosion occurred. With a richer mixture the glow appeared at just under 400° C.: the brown colour disappeared immediately the glow occurred, and the tube was subsequently heated to 530° C. without explosion.

Ethyl nitrate had no apparent effect on the glow but changed the character of the combustion; the cool blue ether flame was replaced by a bright mauve flame, and the quiet wave gave place to an explosion. The glow with ethyl ether-air mixtures was usually less bright than with carbon bisulphide mixtures, but the glow once established persisted although equal volumes of benzene, alcohol, amyl nitrite vapour, etc. (which with carbon bisulphide act as powerful glow inhibitors) were added. Inhibitors of the phosphorescence of ethyl ether were in every case powerful inhibitors with carbon bisulphide.

It will be seen from the chemical data relating to the products of combustion that iron carbonyl does not have a great effect on the combustion results; this corresponds with the relatively small effect on the phosphorescence. The extinguishing action of nitrogen peroxide and bromine appears to be different from that of oxidisable substances such as organic substances or lead tetra ethyl. Similar instances are quoted by Bäckström<sup>10</sup> who points out that the strong inhibitors might have some specific power of depriving the excited molecules of their energy and dissipating it in some physical manner, e.g. in the form of kinetic energy.

Usually it is possible to show that the order of inhibition by substances is directly proportional to the ease of oxidation. In delaying "knocking" in the engine the tertiary amines are less efficacious than the primary or secondary amines, and this can be explained by the fact that the tertiary amines can only be oxidised with the simultaneous destruction of the molecule whereas the primary and secondary amines can be readily oxidised by the simple removal of hydrogen.

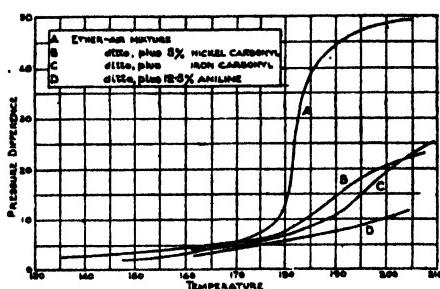
### (c) Results with Acetaldehyde and Amylene.

The aldehydes and amylene phosphoresce similarly to ethyl ether when the vapour is heated in air, the phosphorescence being accompanied by polymerisation and chemical changes into formaldehyde, acetic acid, etc. The first change in the gaseous mixtures on heating was indicated by fog formation and the deposition of dew on the cold exit end of the glass tube, the T.I.C. varying considerably with the mixture strength as shown in Fig. 1. Using the closed bulb method it was possible to follow very slight changes which occurred at still lower temperatures when the time of heating was more than twenty fold that in the glass tube experiments (Figs. 2 and 3).

The phosphorescent flames which with a 28·4 per cent. mixture appeared at 257° and in an 8 per cent. mixture at 305° C. passed slowly along the tube and then became extinguished, but at higher temperatures the flame pulses became more frequent and finally settled down to a steady blue glow

visible only in complete darkness. With amylen-air mixtures phosphorescence and fog formation appeared to coincide, the temperature being that at which the amylen first showed signs of oxidation.

FIG. 2 THE SLOW COMBUSTION OF ETHER IN AIR (CLOSED BULB METHOD)  
WITH AND WITHOUT INHIBITORS

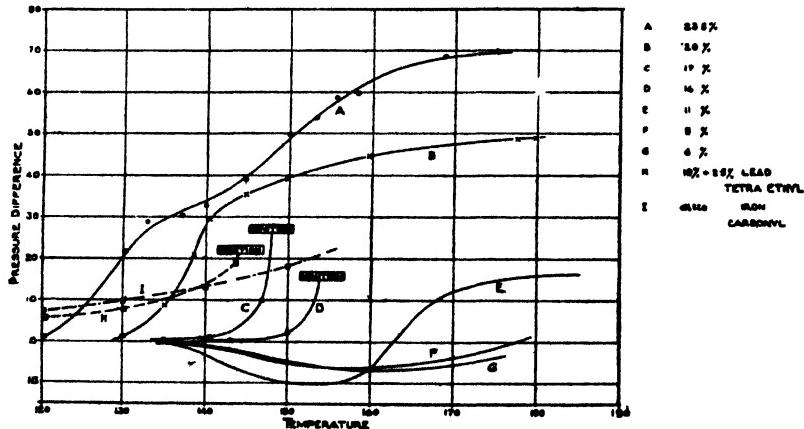


with the addition of lead tetra-ethyl and iron carbonyl (Figs. 2 and 3), which show that the pressure difference begins at a lower temperature but increases much more slowly with rise of temperature. The chemical data in Table VI. relate to the oxidation of acetaldehyde vapour in air at different temperatures with and without iron carbonyl and lead tetra ethyl.

Methane and the vapour of methyl and ethyl alcohols, phenol and benzene were found to have no effect on the acetaldehyde glow. Ammonia

THE SLOW COMBUSTION OF ACETALDEHYDE IN AIR (CLOSED BULB METHOD)  
WITH AND WITHOUT INHIB. TORS.

FIG. 3



caused it first to contract, then to become fluctuating and finally to disappear. Carbon bisulphide and iodine vapour caused the glow to extend slightly, whilst aniline quickly extinguished the glow. Lead tetra-ethyl had no visible effect on the continuous glow, but when admitted to the intermittent combustion waves their temperature as judged by the momentary rise indicated by the thermocouple was slightly reduced. Iron carbonyl quickly extinguished the glow. A small amount of nitrogen peroxide sufficed to extinguish the glow and to raise slightly the temperature at which fog first appeared. Ethyl nitrate delayed the temperature of fog formation by 20°, but caused combustion waves and continuous glow to set in earlier. Ethylene

TABLE VI.—SLOW COMBUSTION PRODUCTS OF ACETALDEHYDE.

Temperature (° C.)	Mixture Strength.	Percentage Amounts by Weight.			
		Carbon Dioxide.	Aldehydes.*	Acids.	Carbon Monoxide.
300	20·5	5·5	11	1·0	16
	10·0	10·0	12	0·6	18
400	21·8	7	10	1·4	—
	11·9	14	13	1·0	—
500	16·4	8·7	7·5	0·5	30
	8·4	10·7	14·0	1·2	—
500 †	15·3	12	12·2	1·8	20
500 ‡	6·3	10	7·0	0·5	30

appeared to be without effect, but carbon monoxide was interesting since it caused the glow to contract and become more intense, as in the experiments on carbon bisulphide. In a later experiment, intermittent combustion was in progress when carbon monoxide was passed into the tube. The waves ceased and gave place to a small bright continuous glow, which suggested that carbon monoxide promoted combustion. Iron carbonyl and carbon monoxide appeared to exert little influence on the glow of amylene in air.

The influence of many metals on the combustion was examined by placing metallic foils, etc., in the tube. With copper, silver, gold, and platinum foils, no effect could be observed, but iron, lead, and thallium all promoted combustion at the metallic surface. If the metals were introduced when intermittent combustion was in progress, a surface glow also appeared. Before each wave the continuous glow gradually increased in intensity and finally spread into the flame itself. Immediately the flame had passed, a weak glow again appeared and the process was repeated.

The action of inhibitors on the phosphorescent glow of acetaldehyde and amylene resembled that on the glow of ethyl ether, suggesting that the mechanism of inhibition is the same or similar for all three. It is known that all these substances are capable of forming peroxides of relative stability which have been isolated.

#### (d) Results with (normal) Hexane.

Hexane vapour phosphoresced in air after the formation of a fog which coincided with the oxidation to aldehydes, acids, water, etc. It was desired to know whether the glow was due to the hexane or to the aldehydes formed during oxidation.

Hexane closely resembled acetaldehyde in the definiteness of its fog formation. A 13·7 per cent. mixture gave a thin fog at 308° C. followed by intermittent combustion waves and rapid thickening of the fog at 314°. When combustion began, the temperature rose spontaneously to about 330° and the thermocouple jumped momentarily to 340° with the passage of each blue flame. The complete absence of red and the prevalence of blue colour seemed to indicate that the fog particles in hexane were of small size.

Nitrogen peroxide caused fog to appear at a temperature 50° below the

\* Calculated as acetaldehyde; this value includes any unchanged acetaldehyde.

† With approximately 0·5 per cent. iron carbon.

‡ With approximately 0·5 per cent. lead tetraethyl.

fog temperature for hexane air alone. It completely prevented the appearance of intermittent combustion waves and continuous glow, but the mixture exploded violently at 43° C. The brown colour disappeared on explosion but returned immediately after. When nitrogen peroxide was admitted to the continuous glow of hexane-air at 35°, the glow disappeared completely.

Ethyl nitrate and carbon bisulphide had no effect on the glow: carbon monoxide caused it to brighten considerably (as with acetaldehyde and carbon bisulphide), whilst ammonia rapidly extinguished the glow. The effect of passing in lead tetra-ethyl with the mixture was to delay the glow from 315° to about 350° and to make the combustion waves much cooler. The "waves" took the form of a faint pulsating glow in the centre of the tube, instead of the intermittent blue flame travelling along it. The action of lead tetra-ethyl on the glow of acetaldehyde was negligible but its effect on the hexane glow was quite marked. Thus when the lead tetra-ethyl was admitted the glow became more diffuse and gradually fainter, and disappeared completely in a few minutes. Iron carbonyl first made the glow feeble and fluctuating, then suppressed it completely. Bromine completely extinguished the glow, as did ethyl alcohol when the air stream was bubbled through the liquid. With a smaller amount of ethyl alcohol, the glow was rendered very faint. Methyl alcohol was less powerful than ethyl. Amyl nitrite, ethyl acetate, ethylene dibromide, and chloroform had the same effect as methyl alcohol, the action of amyl nitrite being quite marked and that of chloroform being much weaker. The hexane glow appeared to be quite unaffected by platinum, gold, silver, copper, aluminium, and tin foils. Thallium, chromium, vanadium pentoxide (used in a porcelain boat) and lead also had little or no effect: and the only apparent effect of an iron strip was to cause the glow to spread over the surface of the iron, the intensity remaining unchanged.

The influence of lead tetra-ethyl, iron carbonyl, aniline, and other inhibitors as well as the action of metals on the chemical changes which occur during the slow combustion of hexane have been already discussed (Callendar, *loc. cit.*). There appears to be a close correlation between the inhibition of phosphorescence and of chemical change.

### Summary.

The results of experiments dealing for the greater part with the inhibitory action of certain substances such as lead tetra-ethyl, iron carbonyl, iodine, ethylene, etc., on phosphorescence and chemical change during slow combustion suggest that peroxidation, occurring at the interface of nuclear particles, is directly responsible for phosphorescence, autocatalysis, and for detonation in the internal combustion engine. Inhibitors, by reacting with the primarily formed peroxides, remove their active oxygen and energy and in this manner destroy the positive catalyst of combustion and cause of phosphorescence and detonation. An important feature of the work is the demonstration that benzene, coal gas, alcohol, ethylene, etc., which can inhibit phosphorescence and delay detonation are autoxidised in the presence of carbon bisulphide, hexane, etc., undergoing incipient combustion, and this provides a further proof of the momentary existence of organic peroxides or of  $\text{CS}_2\text{O}_2$  in the case of carbon bisulphide.

The phosphorescent glow of carbon bisulphide, also self-ignition and slow combustion changes are inhibited by excess of carbon bisulphide. An important point in connection with the mechanism of combustion of hexane is that lead tetra ethyl and ethyl alcohol have a marked action on the glow

and chemical change whereas with acetaldehyde the action is slight. This would seem to indicate that the glow of hexane is not due to the intermediate formation of aldehydes but due specifically to the formation of primary peroxides of hexane.

In experiments carried out by inserting various metals in the combustion tube it was found that the glow usually seemed to be confined to the metal surface which remained unchanged whilst the course of chemical change was altered, there being a considerable decrease in intermediate combustion products and a delay in self-ignition. This inhibitory action of metals is in accord with the view that organo-metallic compounds such as lead tetra ethyl owe their efficacy to the colloidal metal formed by thermal decomposition at the surface of nuclear particles.

Acknowledgment is made to Professor H. L. Callendar, F.R.S., for his inspiring help and supervision.

## PART II. INTERMEDIATE ADDITION-COMPOUNDS AND CHAIN REACTIONS.

### COMPOUND FORMATION IN ESTER-WATER SYSTEMS.

BY JAMES KENDALL AND LILIAN E. HARRISON.

*Received 16th July, 1928.*

The study of the hydration of esters is an important part of the broader problem of the mechanism of acid catalysis of ester hydrolysis. It is generally accepted, at the present time, that the formation of addition compounds in the ternary system  $R\cdot COOR' - HX - H_2O$  constitutes one or more intermediate steps in the process of this hydrolysis. Altogether, four different classes of addition compounds are possible, and these four classes may be listed in the order of their examination.

*Binary Compounds* :  $R\cdot COOR' - HX$ .—The existence of compounds of this type, frequently assumed by earlier investigators, was first established by Kendall and Booge.<sup>1</sup> The complete freezing-point curves of a series of ester-acid systems were examined, a large number of compounds were actually isolated in the crystalline state, and it was shown that their stability in the liquid phase increased regularly, (*a*) with the acidic character of the radical X, and (*b*) with the basic character of the radicals R and R'.

*Binary Compounds* :  $HX - H_2O$ .—Instances of compound formation in acid-water systems have long been known. Most of the familiar acids have been studied more or less carefully, the work of Pickering<sup>2</sup> on the hydrates of sulphuric acid being particularly comprehensive. The results obtained, however, were frequently conflicting, and no general rule regarding such systems was available until it was demonstrated by Kendall, Booge, and Andrews<sup>3</sup> that here also the extent of compound formation was dependent upon the acid character of the radical X. All typical strong acids give definitely isolable hydrates; only by indirect methods can any indication of hydration be obtained in the case of typical weak acids.

*Ternary Compounds* :  $R\cdot COOR' - HX - H_2O$ .—It has been shown by the recent work of Kendall and King<sup>4</sup> that compounds of this type, if existent at all in the ternary mixture, ester-acid-water, are existent only in very minute quantity. This does not, of course, eliminate such compounds as a possible factor in the process of hydrolysis, but it does constitute a bar to the further study of the mechanism of the reaction in this particular direction, since rules regarding the relative stability of such compounds in various systems cannot be formulated. The work of Kendall and King likewise established the fact that binary compounds of the type

<sup>1</sup> Kendall and Booge, *J. Amer. Chem. Soc.*, 1916, **38**, 1712.

<sup>2</sup> Pickering, *J. Chem. Soc.*, 1890, **57**, 64.

<sup>3</sup> Kendall, Booge, and Andrews, *J. Amer. Chem. Soc.*, 1917, **39**, 2303.

<sup>4</sup> Kendall and King, *J. Chem. Soc.*, 1925, **127**, 1778.

$R.COOR'$ — $HX$  are also practically completely decomposed in dilute aqueous solution. The water is evidently to be regarded as a base competing with the ester for the acid, its presence in large excess and its superior strength resulting in the almost total displacement of the ester from its ordinarily stable combination.

*Binary Compounds*:  $R.COOR'$ — $H_2O$ .—These constitute the fourth and final class of compounds to be considered. It was first suggested by Griffith and Lewis<sup>6</sup> that the formation of an ester-water addition compound represented a preliminary stage in the process of hydrolysis, but the fact that the freezing-point depression data for ethyl acetate in water<sup>6</sup> follow almost exactly the ideal curve induced the opinion that such compounds could not be existent in any significant quantity. A more intensive study of the system, however,<sup>4</sup> has led to a reversal of this conclusion. The results of Kendall and King may be summarised in the following quotation:

"Briefly, ethyl acetate is a 'pseudo-ideal' solute in water, two opposing factors practically counterbalancing each other. The fact that ethyl acetate and water are only partly miscible (due to internal pressure differences) precludes all possibility of a normal freezing-point depression curve; the experimental depressions should be considerably less than the ideal (see Hildebrand, 'Solubility,' A.C.S. Monograph Series, 1924). The only factor that could depress the curve back again to correspond with the ideal is extensive compound formation between ester and water, and there are several points which indicate that extensive compound formation actually does occur. Liquids which are partially miscible normally give absorption of heat on admixture, but heat is evolved, not absorbed, when ethyl acetate is dissolved in water. The rapid increase in the solubility of the ester as the temperature is lowered suggests that a compound is formed, the stability of which increases with falling temperature (Hildebrand, *loc. cit.*, p. 144). The fact that the density of the saturated solution at 0° is greater than unity (Seidell, 'Solubilities of Inorganic and Organic Compounds,' D. van Nostrand Co., 1919, p. 285) demonstrates that remarkable contraction accompanies admixture, and this contraction is most simply explained on the assumption of compound formation."

"Other systems of the type  $R.COOR'$ — $H_2O$  are now being examined to discover how these two opposing factors—internal pressure difference and compound formation—vary with the nature of the radicals  $R$  and  $R'$ ."

The present paper gives the first results of this examination. Freezing-point depression and miscibility curves have been determined for aqueous solutions of the following esters: methyl propionate, *n*-propyl formate, ethyl formate, methyl acetate, and dimethyl oxalate. The data for ethyl acetate<sup>7</sup> are also appended for comparison in the diagrams.

The esters were purified by successive fractional distillations from C.P. commercial samples, only those fractions which distilled within 0.1° of the boiling-points as given by Young<sup>8</sup> being retained. The dimethyl oxalate employed melted sharply at 54.35°. All samples were kept in tightly-stopped non-sol bottles in a desiccator until use. Specially distilled water

<sup>6</sup> Griffith and Lewis, *J. Chem. Soc.*, 1916, 109, 80.

<sup>8</sup> Rivett, *Z. physikal. Chem.*, 1912, 80, 547.

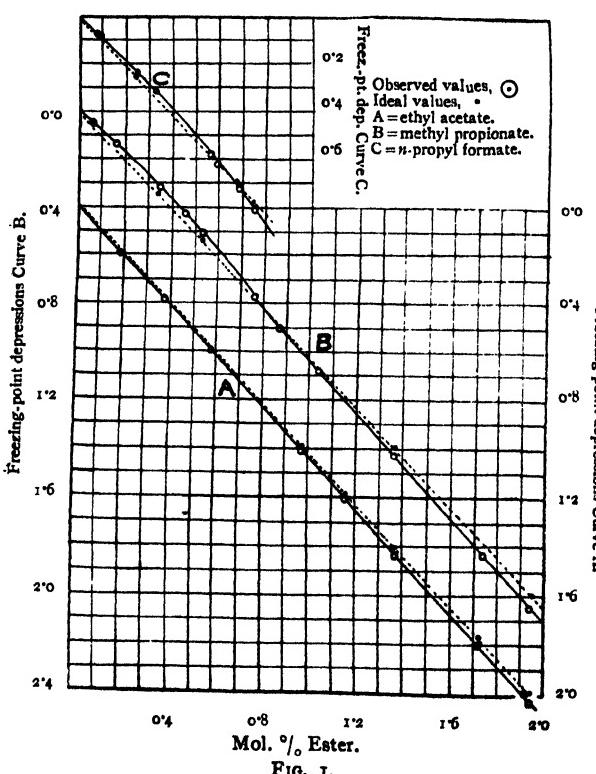
<sup>7</sup> Glasstone and Pound, *J. Chem. Soc.*, 1925, 127, 2660; Kendall and King, *loc. cit.*

<sup>8</sup> Young, *Proc. Roy. Soc. Dublin*, 1910, 12, 374.

was employed in making up the solutions, and both the esters and the water were redistilled from time to time.

For the determination of freezing-point depressions, the ordinary Beckmann apparatus was used, with a thermometer calibrated by the Bureau of Standards. Successive additions of ester were made to a weighed amount of water in the tube by means of a Grethan weight pipette, every precaution being taken to minimise the error due to evaporation of materials during transfer. In the miscibility work, the sealed tube method was adopted,<sup>9</sup> the free space being kept as small as possible in order to avoid any significant change in composition at higher temperatures. Independent work showed that the freezing-point results, with super-cooling restricted to  $0.2^{\circ}$ , could be duplicated to  $\pm 0.001^{\circ}$ , while the miscibility data could be checked, at best, to  $0.1^{\circ}\text{--}0.2^{\circ}$ . Two reasons may be adduced for the low degree of accuracy obtained in the latter part of the work: firstly, the difficulty of observing the exact point at which a second liquid layer just appears or disappears, and secondly, the appreciable rate at which hydrolysis occurs at higher temperatures with certain of the esters (particularly dimethyl oxalate) even in pure water solution.

### Freezing-point Depression Results.



In the following tables, the first line gives the concentration of the solution, expressed in molecular units (mol. per cent. ester). The second line shows the observed depression of the freezing-point, the third the depression calculated from the ideal solution equation,<sup>10</sup> and the fourth the deviation, in thousandths of a degree, of the experimental from the ideal value. The results are also shown in graphic form in Figs. 1 and 2.

<sup>9</sup> Cf. Smith and Eastlack, *J. Amer. Chem. Soc.*, 1916, 38, 1262.

<sup>10</sup> Washburn, "Principles of Physical Chemistry," McGraw-Hill Co., 1912, p. 209.

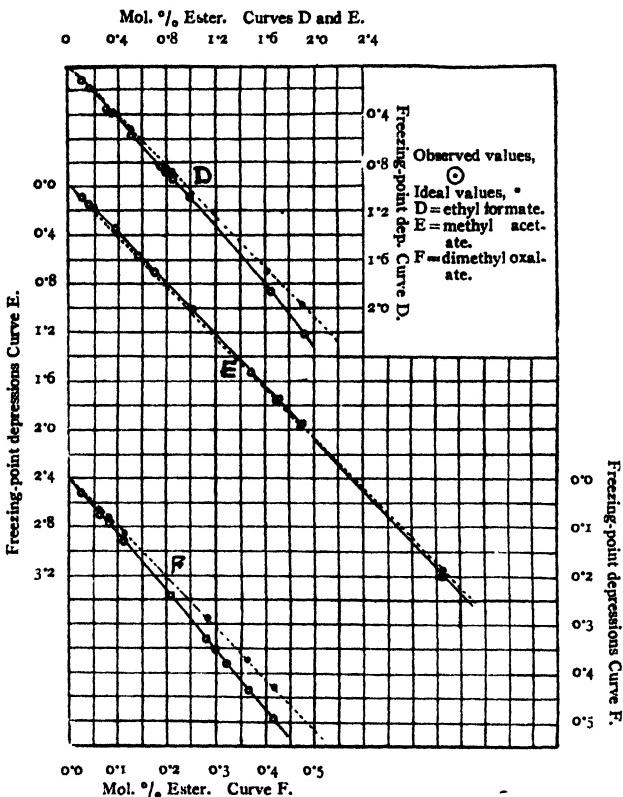


FIG. 2.

TABLE I.—ETHYL ACETATE.

Mol. % Ester	0.181	0.379	0.574	0.963	1.148	1.362	1.718	1.945	2.134
ΔT (obs.)	0.100	0.398	0.594	1.007	1.203	1.437	1.797	2.034	2.224
ΔT (calc.)	0.187	0.391	0.592	0.994	1.185	1.406	1.773	2.007	2.202
Deviation	-3	-7	-2	-13	-18	-25	-24	-27	-22

TABLE II.—METHYL PROPIONATE.

Mol. % Ester	0.065	0.151	0.339	0.451	0.524	0.752	0.862	1.035	1.364	1.748	1.948
ΔT (obs.)	0.059	0.141	0.318	0.425	0.510	0.776	0.896	1.078	1.415	1.828	2.037
ΔT (calc.)	0.067	0.156	0.348	0.465	0.540	0.776	0.890	1.068	1.395	1.803	2.010
Deviation	+8	+15	+30	+40	+30	0	-6	-10	-20	-25	-27

TABLE III.—ETHYL FORMATE.

Mol. % Ester	0.119	0.164	0.311	0.354	0.507	0.757	0.768	0.841	0.976	1.638	1.901
ΔT (obs.)	0.132	0.184	0.343	0.404	0.569	0.837	0.859	0.941	1.082	1.847	2.203
ΔT (calc.)	0.123	0.169	0.321	0.365	0.523	0.781	0.792	0.868	1.007	1.690	1.962
Deviation	-9	-15	-22	-39	-40	-56	-67	-73	-75	-157	-241

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TABLE IV.—*N*-PROPYL FORMATE.

Mol. %, Ester	0·077	0·091	0·248	0·325	0·567	0·600	0·680	0·750
ΔT (obs.)	0·071	0·082	0·236	0·315	0·575	0·620	0·721	0·821
ΔT (calc.)	0·079	0·093	0·255	0·335	0·585	0·619	0·700	0·774
Deviation	+ 8	+ 11	+ 19	+ 20	+ 10	- 1	- 21	- 47

TABLE V.—METHYL ACETATE.

Mol. %, Ester	0·097	0·157	0·182	0·193	0·373	0·562	0·690	0·995	1·476	1·703	1·888	3·045
ΔT (obs.)	0·096	0·139	0·163	0·172	0·355	0·562	0·704	1·023	1·523	1·758	1·950	3·154
ΔT (calc.)	0·100	0·162	0·187	0·199	0·385	0·579	0·712	1·026	1·523	1·757	1·948	3·146
Deviation	+ 4	+ 23	+ 24	+ 27	+ 30	+ 17	+ 8	+ 3	0	- 1	- 2	- 8

TABLE VI.—DIMETHYL OXALATE.

Mol. %, Ester	0·024	0·060	0·081	0·113	0·205	0·280	0·295	0·323	0·362	0·414	0·508
ΔT (obs.)	0·028	0·073	0·095	0·131	0·240	0·330	0·351	0·382	0·432	0·490	0·592
ΔT (calc.)	0·025	0·062	0·083	0·116	0·221	0·289	0·304	0·333	0·374	0·427	0·524
Deviation	- 3	- 11	- 12	- 15	- 19	- 41	- 47	- 49	- 58	- 63	- 68

## Miscibility Results.

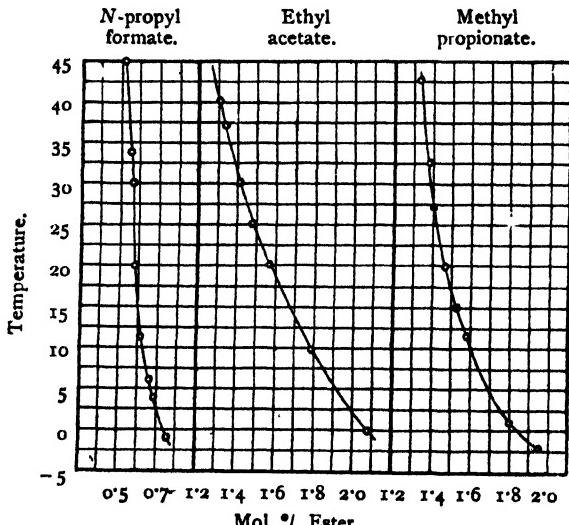


FIG. 3.

As before, the first line in each of the following tables gives the composition of the solution in molecular units. The second line shows the temperature at which saturation (as evidenced by the appearance or disappearance of a second liquid phase, rich in ester) occurs. Figs. 3 and 4 show the results obtained in graphic form.

TABLE VII.—ETHYL ACETATE.

Mol. %, Ester	1·21	1·31	1·34	1·42	1·48	1·58	1·79	2·08
T . . .	50·0	40·0	37·0	30·0	25·0	20·0	10·0	0·0

TABLE VIII.—METHYL PROPIONATE.

Mol. %, Ester	1·33	1·38	1·40	1·47	1·53	1·58	1·80	1·95
T . . .	42·7	32·5	27·1	20·0	14·9	11·5	1·0	- 2·1

TABLE IX.—ETHYL FORMATE.

Mol. % T . . .	1.97 5°	2.05 15.9	2.15 30.2	2.23 38.0	2.31 45.1	2.41 50.0	2.49 55.5	2.73 63.9	2.95 70.0	3.20 75.5
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TABLE X.—N-PROPYL FORMATE.

Mol. % T . . .	0.535 45°	0.555 34.0	0.569 30.0	0.589 20.0	0.620 12.5	0.670 6.0	0.695 4.0	- 0.760 - 1.0
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TABLE XI.—METHYL ACETATE

Mol. % T . . .	6.62 5°	6.70 21.0	6.79 35.0	7.00 58.0	7.03 58.9	7.06 60.1	7.11 61.7	7.51 69.1	7.66 70.5	7.73 71.9	8.83 83.5
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TABLE XII.—DIMETHYL OXALATE.

Mol. % T . . .	0.541 0.1	1.242 11.1	1.853 19.5	2.68 27.1	3.36 31.9	5.36 44.4	6.07 49.2	6.46 51.0	6.91 53.0	8.61 75.0	8.89 79.3	10.22 96.1
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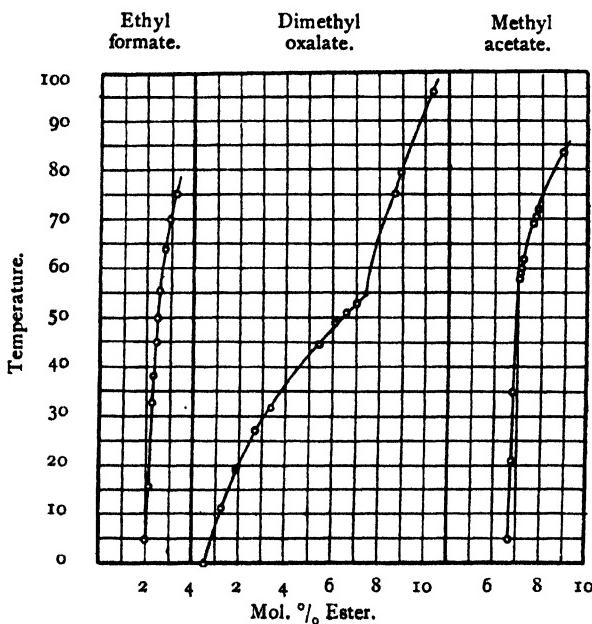


FIG. 4.

**Discussion.**

Before the significance of the results can be examined in detail, it is first necessary to present the figures for the internal pressures of the various esters, since deviations from ideality in any solution are fundamentally dependent upon the relative values for this property possessed by the two components. The internal pressure represents the magnitude of the cohesive

## COMPOUND FORMATION

forces existent between the molecules in the interior of a liquid. It can be calculated in several independent ways, and although the absolute values obtained by different methods for the same liquid may be notably divergent, yet the relative values derived for a series of liquids are essentially the same whatever the method. Since, then, we are interested only in relative values in the present article, the discrepancies in the absolute values evident in the following table need not disturb us.

In this table, the internal pressures in atmospheres at 20° are calculated by four distinct methods.<sup>11</sup> The first method is based upon an equation derived by Stefan<sup>12</sup> connecting internal pressure with heat of vaporisation; the second upon Van der Waals' equation, the values for the "constant"  $a$  being averaged according to Mathews;<sup>13</sup> the third upon the equation derived therefrom by Benedicks,<sup>14</sup> involving the coefficient of expansion; and the fourth upon a more complex equation of state proposed by Sutherland.<sup>15</sup> The figures in the first three columns of the table purport to be absolute values, those in the fourth are frankly relative. The values for ether are added for comparison.

TABLE XIII.—INTERNAL PRESSURES (ATMOSPHERES) 20°.

Liquid.	From Heat of Vaporisation.	From Van der Waals' Eqn.	From Coeff. of Expansion.	From Sutherland's Eqn.
Ethyl ether . .	1240	1600	930	405
Ethyl acetate . .	1585	2370	1115	500
Methyl propionate . .	1650	2430	1150	515
<i>N</i> -propyl formate . .	1615	2440	1160	530
Ethyl formate . .	1755	2770	1340	575
Methyl acetate . .	1800	2740	1330	560
Dimethyl oxalate . .	2040	—	—	—

It will be evident that all of the esters included in the above table have internal pressures significantly higher than that of ether, and that they may be divided into three groups: (*a*) the isomers ethyl acetate, methyl propionate and *n*-propyl formate, with approximately equal low internal pressures; (*b*) the isomers ethyl formate and methyl acetate, with approximately equal intermediate values; and (*c*) dimethyl oxalate, with a relatively high internal pressure. The single value obtainable for dimethyl oxalate refers, of course, to the substance in the liquid state. The values for water given in the literature range from 5000 to 37,000 atmospheres, however, so that abnormalities due to internal pressure differences may be anticipated to occur in all binary mixtures. We may now proceed to study the actual experimental curves.

The miscibility data will be considered first. Figure 3 shows that the three esters with low internal pressures are all only slightly soluble in water and that all exhibit retrograde solubility. The increase in solubility with decrease in temperature is most rapid in the case of ethyl acetate, which has the lowest internal pressure. Figure 4 indicates that the two esters with intermediate internal pressures are more soluble in water, that

<sup>11</sup> Compare Hildebrand, *J. Amer. Chem. Soc.*, 1919, 41, 1067; "Solubility," pp. 99-116.

<sup>12</sup> Stefan, *Wied. Ann.*, 1886, 29, 655.

<sup>13</sup> Mathews, *J. physical Chem.*, 1913, 17, 603.

<sup>14</sup> Benedicks, *Z. anorgan. Chem.*, 1905, 47, 455.

<sup>15</sup> Sutherland, *Phil. Mag.*, 1893, 35, 211.

their solubility is almost independent of temperature below 50°, and that only above 50° does a significant increase in solubility with temperature begin to become evident. Dimethyl oxalate, on the other hand, with the highest internal pressure, shows a rapid increase in solubility with temperature both in the solid and in the liquid phases, although it must be admitted that the results above 60° are only approximations owing to rapid hydrolysis. The break in the curve occurs at 53·4°, about one degree below the melting-point of the pure ester.

It is interesting to note for purposes of comparison that di-ethyl ether, with an internal pressure considerably lower than ethyl acetate, exhibits a solubility curve in water even more sharply retrograde than that of the ester. It would appear that internal pressure differences between solvent and solute may be a preponderating factor in determining the nature of the solubility curves in systems of similar character. However, our present knowledge of this field does not admit of any broad generalisation or any final explanation of the experimental results. When we remember that an ideal liquid mixture demands perfect miscibility, it is clear that the curves become uniformly more abnormal the greater the difference between the relative internal pressures of the ester and water. Until we know how internal pressure varies with temperature, however, in each particular case, it is dangerous to speculate further.

When we turn to the freezing-point depression data in Figures 1 and 2 the course of the curves with respect to the ideal is seen to differ somewhat for the different esters, although large deviations occur only at concentrations approaching the saturation point. All of the curves can be logically explained under the assumption of two counterbalancing factors—internal pressure differences tending to induce an abnormally small depression, and compound formation tending to induce an abnormally large depression. For ethyl acetate, these two factors almost exactly neutralise one another, and the curve falls only slightly below the ideal over its whole length. In three of the esters here examined, however, the internal pressure or "immiscibility" factor is sufficiently powerful at lower concentrations to preponderate, the curves for methyl propionate, *n*-propyl formate and methyl acetate showing positive deviations in their early stages. For ethyl formate and dimethyl oxalate, on the contrary, the compound formation factor is preponderant throughout, the deviations of the experimental results from the ideal being uniformly negative and increasing rapidly at the higher concentrations. Even in the case of the other three esters, the curves cross the ideal as the concentration is increased, and the abnormally high depressions obtained in all instances in the neighbourhood of saturation offer indubitable evidence of the extensive nature of compound formation between the ester and water in the solution.

It is apparent, on examination, that the greatest negative deviation in the freezing-point curves at comparable concentrations is given by dimethyl oxalate, and the next greatest by ethyl formate and *n*-propyl formate, while ethyl acetate, methyl acetate and methyl propionate are much closer to the ideal. From this it would seem that the factor which determines the extent of compound formation is the character of the *acid radical* of the ester. The ester with the strongest acid radical, dimethyl oxalate, gives the strongest indications of compound formation, the formate esters follow next, and the esters with the weak acetate and propionate radicals are all relatively near together at the end of the list. Little difference can be seen between esters differing only in their alcohol radical; its character appears to be of much minor importance.

A very significant point may here be noted. It has long been known<sup>16</sup> that the speed of ester hydrolysis in acid solutions is similarly dependent upon the character of the acid radical of the ester, esters of strong acids being much more rapidly hydrolysed than esters of weak acids, while the nature of the alcohol radical is again a very minor factor. The temptation is obvious to conclude that the speed of the hydrolysis is conditioned by the concentration of ester-water compound present in the solution, and that the suggestion of Griffith and Lewis that the formation of such compounds is a necessary preliminary step in the process of hydrolysis has received strong confirmation. While it would be advisable to experiment with a greater number of esters before drawing any general conclusions of this nature, such an expansion of data would be difficult, since the higher esters are so insoluble in water as to make them unsuitable for this type of work.

### Summary.

The freezing-point depression and miscibility curves of the following esters in water have been examined: ethyl acetate, methyl propionate, *n*-propyl formate, ethyl formate, methyl acetate and dimethyl oxalate. Critical analysis of the results obtained shows that the course of the miscibility curve depends primarily upon the internal pressure of the ester. Compound formation is extensive in all systems, and increases with the strength of the acid radical of the ester. The speed of ester hydrolysis in acid solutions is known to depend similarly upon the same factor, and further correlation of the two phenomena will be attempted in subsequent articles.

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<sup>16</sup> Löwenherz, *Z. physikal. Chem.*, 1894, 15, 389.

## REPORT ON THE THEORY OF CHAIN-REACTIONS.

By J. A. CHRISTIANSEN.

*Received 30th July, 1928.*

It is well known that the chemical reactions which we observe are, as a matter of fact, very often resultants of several components which are to be considered as the elementary reactions, the reactions which cannot be further resolved.

Furthermore, it is well known that certain bimolecular reactions follow a very simple law, in so far as their velocity can be expressed as follows:—

$$v_{12} = C_1 \cdot C_2 \cdot r_{1,2} e^{-\frac{Q_{12}}{RT}} \quad \dots \quad \dots \quad \dots \quad \dots \quad (1)$$

where  $r_{1,2}$  is a factor which does not differ much from the factor  $s_{1,2}$  in the equation for the number of collisions  $c_{1,2}$  between the same molecules—

$$c_{1,2} = C_1 \cdot C_2 \cdot s_{1,2} \quad \dots \quad \dots \quad \dots \quad \dots \quad (2)$$

$C_1$  and  $C_2$  are the concentrations and  $Q_{12}$  very nearly equal to the heat of activation.

On the other hand, Herzfeld<sup>1</sup> has given a quantitative theory of the

<sup>1</sup> K. F. Herzfeld, *Ann. Physik*, 59, 635 (1919).

velocity of a bimolecular elementary reaction leading just to the expression (1) with

$$r_{1,2} = s_{1,2} \dots \dots \dots \quad (3)$$

He uses the special assumption that the condition for reaction is that the two molecules collide with a relative velocity along the axis in the moment of collision which exceeds a certain limit. Other assumptions may lead to a similar result, but I am not going to enter into detail on this point. The interesting fact is that the empirical results agree with the theory for elementary reactions, thus showing that what has been measured is, in the cases cited, essentially the velocities of the corresponding elementary reactions.

From equations (1) and (3) we see that the velocity of the elementary reaction is completely determined by (a) the concentration of the reacting molecules and (b) by the temperature function  $r_{1,2} e^{-\frac{Q_{1,2}}{RT}}$ . This latter expresses the frequency with which certain characteristic combinations of molecules 1 and 2 occur in the gas at unit concentrations, *i.e.* it is an expression of the distribution of the molecules or pairs of molecules in the different possible states.

Quite generally we may state that the velocity of an elementary reaction is given by the concentrations of the reactants and their distribution.

It is a question of some interest to ascertain whether this distribution is the same as that which would exist if the reaction were not proceeding. When only molecules in non-reactive states are considered, this is certainly so to a high degree of approximation. Concerning the reactive molecules the question is not so easily answered. In solution, the Maxwell-Boltzmann distribution of the solute is, to a great extent, effected by the abundant solvent molecules, and consequently the deviation from the normal distribution cannot be great. In a gas, on the other hand, the deviations may be greater as the collisions, which serve to transfer the molecules to the states in which reactions may occur, are more or less the same as those at which the reactions actually occur, so that evidently the equilibrium concentration of "active molecules" cannot be reached.<sup>2</sup> However, in the course of time a state will be reached in which the concentration of active molecules becomes stationary. It can very easily be shown that in a simple case this state will be reached in a time which is comparable with the average lifetime of an activated molecule, *i.e.*, which is short as compared to a second.<sup>3, 3a</sup> This state will furthermore be stable, as an artificially produced increase in the concentration of active molecules will create a tendency for the concentration to decrease with time, while, on the other hand, a decrease will create a tendency for it to increase with time. If we assume as a very natural assumption that this state has the greatest probability consistent with the given parameters and the reaction which is an inevitable event in certain systems, then it seems probable that we may be able to treat the reaction velocity as a thermodynamic problem. I shall return to this point in a later paper.

However, we can state that the velocity of a certain elementary reaction must be given solely by the amounts of the different substances and the distribution function. In a symbolic way we can write

$$v = \sum_s n(s) \cdot p(s)$$

<sup>2</sup> See for example *Z. physik. Chem.*, 104, 451 (1923).

<sup>3</sup> R. H. Fowler and E. K. Rideal, *Proc. Roy. Soc., A.* 113, 570 (1927).

<sup>3a</sup> *Z. physik. Chem.*, 128, 430 (1927).

where  $n$  means the number of molecules or complexes of molecules in the different states and  $p(s)$  the probability per second for reaction in the  $s$ th state. It must be remarked that the function  $n(s)$  may not be the same as the one found in the static case.<sup>4</sup> However, it is seen that only by variations of the distribution function can  $n$  be varied as  $p(s)$  must be a function of the condition alone. Furthermore, it must be remarked that the equation holds good only in the case of one elementary reaction. Now it is a well-known result from thermodynamics that small amounts of a foreign substance added to a solution in which equilibrium has been established, cannot alter the distribution function to any appreciable extent. This is a direct result of the fact that the free energy is a maximum in the equilibrium state so that disturbances which are infinitely small of the first order can only alter the free energy by infinitely small quantities of a higher order. Now from the above considerations it follows directly \* that the reaction velocity also has maximum properties and so the same will be true of this also, that is, small disturbances can only produce in the reaction velocity small changes of a higher order. This result is quite general but it must be remembered that it holds good for each elementary reaction separately. In the case of a more complicated reaction which consists of at least two consecutive elementary reactions which form a reaction chain, for example

$\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$ ,  $\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}$ , and so forth, the case may be that one reactant or resultant has a very small steady state concentration, and in this case "small" disturbances means the addition of quantities of substances which are small also as compared with the quantities of this component.

We can thus state that the velocity of an elementary reaction is independent of small amounts ( $m$ ) of foreign substances in the solution, i.e.

$$\lim_{m \rightarrow 0} \frac{dv}{dm} = 0.$$

This equation, however, does not exclude catalysis, as it might seem to do, but it shows that when small † amounts of a foreign substance ( $a$ ) increase the velocity of a certain stoichiometric reaction, then other ways of reaction have been opened, i.e., other elementary reactions take place. For even if the reaction really is a complex of several elementary reactions then a stable velocity will be one which cannot by itself increase further. With regard to unstable velocities I shall say a few words later. On the other hand, when small amounts of a foreign substance ( $b$ ) decrease the velocity, we must conclude that the reaction is complex and so that at least one of the intermediate substances essential for the reaction is to a *relatively* great extent removed in some way or another by the added substance.

The matter becomes more easy to understand when we express it thus : We get negative catalysis when the reaction is a chain reaction in which the chains are broken by the addition of a foreign substance <sup>5, 2, 6, 7</sup>. But it must be remembered that the latter way of expressing the matter is not correct in all

\* I shall revert to this in a later paper, as very important consequences can be drawn herefrom.

† "Small" as compared with the known quantities of the reactants.

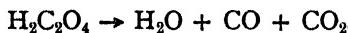
<sup>4</sup> Z. physik. Chem., 104, 1923, see note 1 on p. 456.

<sup>5</sup> J. A. Christiansen : Reaktionskinetische Studier, Dissertation, Copenhagen, 1921, p. 65.

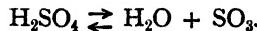
<sup>6</sup> J. physical Chem., 28, 145, 1924.

<sup>7</sup> Compare also F. Perrin, Compt. rend., 184, 1121 (1927).

cases of "negative catalysis." For instance, certainly not in the dissociation of oxalic acid dissolved in sulphuric acid<sup>8</sup> according to the equation



In this case it seems that we measure some reaction between oxalic acid and  $\text{SO}_3$  or some other "sulphuric acid" which is less hydrated than  $\text{H}_2\text{SO}_4$ . If for example we add small amounts of water, then the reaction is highly retarded. If, on the other hand, we add  $\text{SO}_3$  it is highly accelerated, so that in this case we have to do with a simple displacement of, e.g., the equilibrium



In this case the more general statement (*b*) is obviously correct.

I shall now discuss some features of chain reactions from a general point of view. The first well-known example of a chain reaction was ascertained by Bodenstein in the photochemical reaction between hydrogen and chlorine. The reaction had been investigated partly by Chapman<sup>9</sup> in Oxford and partly by Bodenstein<sup>10</sup> and Dux in Hanover.

It shows a very marked negative catalysis, as the velocity is inversely proportional to the oxygen content of the gas. Bodenstein<sup>11</sup> set forth a special chain mechanism which, although it proved to be wrong, all the same gave the essentials of the general theory. Nernst<sup>12</sup> later on proposed the "atomic chain" theory mentioned above, which seems to explain all the details of the reaction. But the thermal reaction between  $\text{H}_2$  and  $\text{Cl}_2$  was also found in Bodenstein's laboratory<sup>13, 14</sup> to show negative catalysis by oxygen, and later on many examples were found, in particular the auto-oxidation of organic aldehydes investigated by Moureu<sup>15</sup> and coworkers. These reactions are strongly inhibited by very small amounts of oxidisable substances as, e.g., hydroquinone, and must consequently, according to our theory, be chain-reactions. In this case, for example, there is no possibility of displacement of an equilibrium by which the concentrations of the original reactants may be altered. That the theory is correct was proved by Backström<sup>16, 17, 18</sup> by very direct experiments carried out partly in Taylor's laboratory at Princeton and partly in Stockholm. Backström found, for example, that the reactions were photosensitive and gave a quantum yield of often tens of thousands. Moreover, the photochemical reactions were inhibited by the same substances as the thermal ones, and at least in some cases according to the same law. To understand these results we may try to calculate the form of the velocity curve. Let the number of reactions started per second be  $N$  and let the number of links in each chain be  $L$ , then of course the velocity  $v$  must be

$$v = N \cdot L$$

<sup>8</sup> Bredig and Lichty, *Z. Elektrochem.*, **12**, 459 (1906).

<sup>9</sup> Chapman and McMahon, *J. Chem. Soc.*, **95**, 959 (1909).

<sup>10</sup> *Z. physik. Chem.*, **85**, 297 (1913).

<sup>11</sup> For a full bibliography down to 1926 see *Fortschritte der Chemie, Physik, und physikalische Chem.*, **18**, II : *Dic Chloralkaligasreaktion von Nathaniel Thon*.

<sup>12</sup> *Z. Elektroch.*, **24**, 335 (1918).

<sup>13</sup> K. Sachtleben, *Dissertation Hannover*, 1914.

<sup>14</sup> M. Bodenstein and H. S. Taylor, *Z. Elektroch.*, **22** (1916), p. 53.

<sup>15</sup> For a complete report see C. Moureau and Dufraisse "Reports of the Solvay International Council on Chemistry," Brussels, April, 1925.

<sup>16</sup> *J. Amer. Chem. Soc.*, **49**, 1460, 1927.

<sup>17</sup> *Medd. Nobel Inst.*, *Stockholm*, **6**, No. 15, 1927.

<sup>18</sup> *Ibid.*, **6**, No. 16, 1927.

if the chains do not interfere with each other. This latter assumption will be true, when the chains are not excessively long and we shall assume it as a first approximation. Now let us assume that the probability that one elementary reaction shall induce another is  $P$ . Then obviously the number of links will be

$$L = 1 + P + P^2 \dots$$

which sum is equal to  $1/(1 - P)$  if  $P < 1$ . We shall mainly consider this case. Now, as is well known, the explanation of the chain is, that some one of the resultants is in some way "active," i.e., it is either a very reactive molecule or atom as in the reaction between hydrogen and chlorine, or it may be some excited molecule as Bäckström<sup>18</sup> has assumed. These active resultants now activate one of the reactants or it becomes de-activated. This de-activation may occur either independently on the inhibitor or by some reaction (transference of energy or chemical reaction) with it. We may classify these two possibilities as "spontaneous" and "induced" de-activation. Consequently

$$P = \frac{k_r \cdot C_r}{k_r \cdot C_r + k_i C_i + k_s}$$

where index  $r$  refers to reaction,  $i$  and  $s$  to induced and spontaneous de-activation respectively. We thus get

$$v = N \cdot L = N \frac{k_r \cdot C_r + k_i C_i + k_s}{k_i C_i + k_s}$$

When the chain is very long the expression reduces to

$$v = N \cdot \frac{k_r C_r}{k_i C_i + k_s}$$

Very often the expression for  $P$  is more complicated. For instance in the  $H_2$ ,  $Cl_2$  reaction it is a product of two factors each similar to our  $P$ . Backström<sup>16</sup> found empirically a relation of the form:

$$v = \frac{v_0}{C_i + B}$$

where  $B$  is a constant. This equation is exactly equivalent to the above. As Backström himself is going to give a report here, I shall not enter in more detail on his work.

I must here make one general remark. The method of calculation used above may easily be applied to the simpler cases. It is exactly equivalent to the method of stationary velocity which is so often used in kinetics, e.g., by Bodenstein and coworkers.<sup>3a</sup> In the more complicated cases the latter method becomes the more convenient. Also it has the advantage of showing one point more clearly, namely, that in the case of negative catalysis the very small concentrations of the active intermediate products are strongly influenced by the inhibitor. Consequently the general remark, p. 597, applies to this case and we have also here to do with displacement of a stationary distribution.

We may now consider the cases where  $P$  may be greater than unity. This is not at all excluded as the energy with which the resultants leave the reaction may be quite sufficient to start more than one new reaction. To discuss the matter in general we may use the following formula, which has been developed<sup>2</sup> from rather general view-points:—

$$v = \frac{F(C)}{P_i + A(1 - a)}$$

Here  $A(C)$  is a function of the concentrations and  $p_i$  another function of the concentrations, which corresponds to the probability of spontaneous deactivation mentioned above. The introduction of  $p_i$  has been shown to be necessary for thermodynamic reasons.  $A$  is a constant which is as a rule many times (e.g.  $10^5$ ) greater than  $p_i$ , and  $a$  a fraction which measures the ratio between the number of cases in which an active reaction product activates another reactant during its being deactivated and the total number of cases in which it is deactivated by a collision with the reactant.

We may now distinguish between three cases: (1)  $a = 1$ . In this case, the velocity is stable and we may assume that in a certain case it is measurable. If now (2)  $a$  becomes appreciably smaller than unity, then  $v$  becomes very small, as the term  $A(1 - a)$  now becomes predominant. If  $a$  becomes a little greater than 1 but so that the denominator is still positive, we shall have essentially the case (1) only with still greater but stable velocities. Finally, if (3)  $p_i + A(1 - a) < 0$  the velocity becomes unstable and the reaction proceeds with ever-increasing velocity until the concentrations have altered so much that again  $a < 1$ , in which case the reaction practically stops, even if the reactants are not totally used up. That such cases really exist has recently been rediscovered by Semenoff in Leningrad who showed that oxygen in very small concentrations 0.01-0.0001 mm. practically does not react with phosphorus.<sup>19, 20, 21</sup> I regret that space does not allow me to enter on these highly interesting investigations.

It is obvious that the three stages mentioned above roughly correspond to the empirical results on gaseous explosions. According to the composition of the gas and the temperature we may have either no ignition (*vide* case (2)), the slow combustion wave (*vide* case (1)), or the very fast explosion wave (*vide* case (3)). It seems as though case (1) (stable and measurable velocity) has been realised by C. N. Hinshelwood in his beautiful experiments in the system hydrogen-oxygen, but on these it is quite unnecessary to enter as Dr. Hinshelwood himself has reported on this.

<sup>19</sup> *Z. Physik.*, **48**, 571, 1928.

<sup>20</sup> The phenomenon was originally found by Joubert (*Ann. scient. de l'École Norm. Sup.*, **3**, p. 209 (1874)), and was studied later on by Lord Rayleigh, *Proc. Roy. Soc., A.*, **99**, 372 (1921).

<sup>21</sup> A very complete bibliography has been given by H. Bäckström (*Ref. 18*).

## THE MECHANISM OF INHIBITION IN AUTO-OXIDATION REACTIONS.

BY HANS L. J. BÄCKSTRÖM.

*Received 3rd September, 1928.*

In a paper published last year,<sup>1</sup> I gave some results obtained in a study of three typical reactions showing negative catalysis, *viz.* three auto-oxidation reactions. I was able to show that in all cases the photochemical reaction is a chain reaction, and that the substances which inhibit the thermal reaction have a similar effect on the photochemical reaction. In agreement with Christiansen's theory of negative catalysis, the results indicated, therefore, that the thermal reaction, also, is a chain reaction, and

<sup>1</sup> Bäckström, *J. Amer. Chem. Soc.*, **49**, 1460 (1927).

that the rôle of the inhibitor, in the thermal as well as in the photochemical oxidation, consists in the breaking of reaction chains.

The results obtained in the auto-oxidation of sodium-sulphite solutions containing different alcohols as inhibitors were particularly striking as they revealed a quantitative agreement between thermal and photochemical reaction. They could be represented by the formulæ:—

$$V_d = \frac{k_1}{kC + k_2}; \quad V_i = k_3 V_d = \frac{k_3 k_1}{kC + k_2},$$

where  $V_i$  = light rate,  $V_d$  = dark rate,  $C$  = concentration of alcohol, and  $k_1$ ,  $k_2$ ,  $k_3$  and  $k$  are constants. The value of  $k$  depends on the nature of the alcohol, and is a measure of its relative inhibitory power. The formulæ express the facts that, under a given set of experimental conditions, the ratio between the rates of light and dark reaction remain constant, independent of the nature and concentration of the alcohol present, and that both rates are inversely proportional to a sum of two quantities, one being a constant,  $k_3$ , and the other proportional to the concentration of the inhibitor. The form of the equations and the complete analogy between light and dark reaction which they reveal, indicate that the presence of the alcohols does not in any way affect the number of chains started per unit time, but that they act solely by breaking the reaction chains.

The other reactions studied gave results that were similar, although not quite as simple.

The question then arises: what is the mechanism by which the chains are broken by the inhibitor? This is a problem of considerable interest since this mechanism must obviously be closely connected with the mechanism of chain propagation. In a preliminary discussion of this problem in a more recent paper,<sup>2</sup> I reached the conclusion that the mechanism by which the chains are broken is probably an induced reaction between the inhibitor and one of the reactants. In favour of this view I may cite the work of Moureu and Dufraisse<sup>3</sup> on the oxidation of acrolein and other organic liquids which shows that the inhibition does not last indefinitely, but that the oxidation sets in sooner or later, indicating that the inhibitor is eventually destroyed. Furthermore, as I pointed out in that paper, this would account for the relationship which seems to exist in the slow combustion of phosphorus between the maximum oxidation pressure and the formation of ozone which accompanies this reaction. It may also be recalled that, apparently, the same applies to the only case of inhibition of a *photochemical* chain reaction that has been closely investigated, namely the inhibition of the hydrogen-chlorine combination by oxygen. This reaction is accompanied by the formation of water and, as first suggested by the Chapmans,<sup>4</sup> the experimental facts may be interpreted as indicating that it is this induced, or "photosensitized," reaction which causes the chains to be broken.

From this point of view the results of Bigelow<sup>5</sup> on the inhibitory power of the four butyl alcohols in the oxidation of sulphite solutions are significant. He found that the primary, the secondary, and the iso-butyl alcohols, all acted as inhibitors, but that the tertiary had no effect. Since the first three alcohols can be easily oxidized to aldehydes and ketones, whereas the tertiary can only be oxidized with the simultaneous destruction of the

<sup>2</sup> Bäckström, *Medd. K. Vet.-Akad. Nobelinst.*, 6, No. 16 (1927).

<sup>3</sup> Moureu and Dufraisse, *Compt. rend.*, 174, 258 (1922), and subsequent papers.

<sup>4</sup> D. L. and M. C. C. Chapman, *J. Chem. Soc.*, 123, 3079 (1923).

<sup>5</sup> Bigelow, *Z. physik. Chem.*, 26, 493 (1898).

molecule, there seems to be a direct relation between inhibitory power and oxidizability in this case;<sup>6</sup> and the logical conclusion seems to be that the alcohols are actually oxidized in the process of breaking the reaction chains. Without postulating any special mechanism of chain propagation, the reaction chain may be described as a series of processes whereby the oxidation of one sulphite ion induces the oxidation of another, and so on. The assumption would be, then, that in the presence of the alcohol this sometimes leads, instead, to an induced oxidation of an alcohol molecule, and that this reaction is incapable of inducing further oxidations or, at least, is less efficient than the corresponding reaction involving a sulphite ion.

To test this idea of a relation between inhibition and induced reactions, a series of investigations have been undertaken at Princeton. The first of these has just been completed, and I shall give a brief account of the results obtained.

For this investigation, which was carried out in collaboration with Mr. Hubert N. Alyea, the oxidation of sulphite solutions in the presence of alcohols was selected, since my previous work had indicated that this represents an unusually simple case of inhibition, and also because this is a relatively simple system from an analytical standpoint, the auto-oxidizable substance being an inorganic salt whereas the inhibitors and their transformation products are organic substances. Isopropyl, sec.-butyl, and benzyl alcohols were tried as inhibitors, and in agreement with the theory it was found that they were oxidized to acetone, methyl-ethyl ketone, and benzaldehyde, respectively. The amounts of these substances that were formed were extremely small—as was to be expected on the theory—but Mr. Alyea succeeded in increasing the sensitivity of existing colour tests about ten times, which rendered quantitative determinations possible.

Let us now see what quantitative results we should expect on the theory, and compare them with those obtained experimentally.

The fact that, as shown by the formulæ, the chain length is inversely proportional to the factor,  $kC + k_2$ , shows that the chains may be broken in two ways: (i) by the alcohol, its activity in breaking the chains being proportional to its concentration,  $C$ , and its relative inhibitory power,  $k$ ; or (ii) due to some other cause represented by the constant  $k_2$ . We are at present concerned only with the former of these two processes.

If we make the assumption that the induced oxidation of the inhibitor is completely incapable of inducing further oxidations, *i.e.*, always breaks the reaction chain, then we should expect that every chain which is broken by the alcohol gives rise to the formation of one molecule of the oxidation product, *e.g.*, acetone in the case of isopropyl alcohol. If we call the total number of chains started and broken per minute  $n$ , the number of chains broken in that time by the alcohol will be  $n \left( \frac{kC}{kC + k_2} \right)$ , and this number of acetone molecules will be formed per minute. Since the velocity of sulphite oxidation,  $V$ , is expressed by the formula  $V = \frac{k_1}{kC + k_2}$ , it follows that the amount of acetone formed in a given time will always be proportional to  $CV$ , the product of reaction velocity and inhibitor concentration.

At small inhibitor concentrations this product increases with increasing values of  $C$ , and the rate of acetone formation should increase in proportion.

<sup>6</sup> Compare the theories of Dhar, *Proc. Acad. Amsterdam*, **23**, 1074 (1921); *Z. anorg. Chem.*, **122**, 146 (1922), and Moureu and Dufraisse, *Compt. rend.*, **176**, 624 (1923), linking inhibitory power and oxidizability.

At large inhibitor concentrations, on the other hand, where  $k_2$  is negligibly small compared to  $kC$ , this product becomes virtually constant, independent of the alcohol concentration. In this region practically all the chains are broken by the alcohol. Increasing the alcohol concentration causes the chains to be broken sooner, and therefore lowers the rate of sulphite oxidation, but the *number* of chains broken remains the same, and the amount of alcohol oxidized in a given time should therefore remain constant, independent of its concentration.

That this is true is shown by Fig. 1, which represents the data for benzyl alcohol. In the upper graph,  $CV$  is plotted against the logarithm of the concentration, the latter being expressed in moles per litre and the reaction velocity in moles per litre per hour. The lower graph gives the amounts of benzaldehyde formed per hour, plotted in the same manner. The full-drawn curve in the upper graph was obtained from the formula

$$V = \frac{0.00029}{C + 0.0012}, \text{ the one in the lower graph from the same expression multiplied by a constant factor.}$$

Obviously, it is another consequence of the theory that, within the region

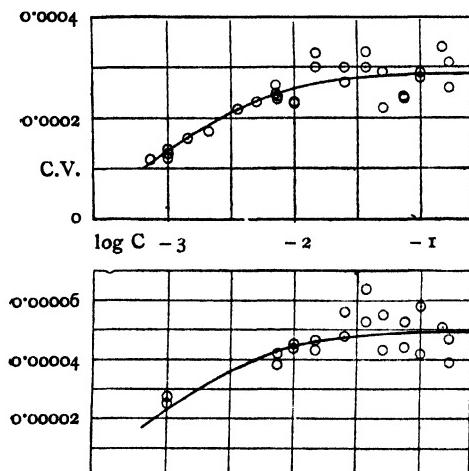


FIG. 1.—Benzaldehyde.

where all the chains are broken by the alcohol, the number of alcohol molecules oxidised in unit time should be the same for different alcohols. The only difference will be that the amounts of these which have to be added in order to reach this region will vary inversely as their specific inhibitory powers,  $k$ . This is shown by Table I., which summarises the data for the three alcohols studied. Column 2 gives the range of concentrations within which  $CV$ , as well as the rate of the induced oxidation, were found to be constant within

limits of error. Column 3 gives the average  $CV$ -values within that range, column 4 the corresponding values of  $k$ , and the last column the average amounts of the oxidation products formed, in moles per litre per hour.

TABLE I.

Alcohol.	Concentration Range, Moles/Litre.	$CV \times 10^4$ .	Inhibitory Power, $k$ , (from $CV$ ).	Oxidation Product Formed.	Rate of Induced Oxidation, Moles/lit./hour.
Isopropyl	0.05 – 1.5	34	3.0	Acetone	0.000046
Sec.-butyl	0.15 – 1.8	103	1	Methyl-ethyl ketone	0.000049
Benzyl	0.0073 – 0.167	2.8	37	Benzaldehyde	0.000048

When two alcohols are present in the solution at the same time, they should be oxidized in proportion to their concentrations and relative

inhibitory powers, but the total number of molecules oxidized in a given time should still be the same. This was verified for an equi-molar mixture of benzyl and isopropyl alcohols. The total number of moles oxidized per litre per hour was 0.000044, the two alcohols sharing in this total in the ratio of 13 : 1. The *CV* values of Table I. give a ratio of the inhibitory powers of 12 : 1.

The applicability of the theory to the photochemical reaction was tested in a series of experiments with isopropyl alcohol. The light source was a mercury arc which was used with a chlorine-bromine filter. Just as with the thermal reaction, it was found that both *CV* and the rate of acetone formation were independent of the concentration of the alcohol over the range 0.05 – 1.5 moles per litre. As was to be expected, illumination increased the rates of both reactions in the same proportion: *CV* from 0.0034 to 0.051, *i.e.*, in a ratio of 1 : 15.0; the rate of acetone formation from 0.000046 to 0.00066 (= 1 : 14.3). This shows that in a solution of a given composition the chain length is the same whether the chains are started thermally or photochemically.

The chain length may, however, also be obtained in a different and altogether independent way, *viz.*, from quantum efficiency measurements on the photochemical reaction. If the absorption of a light quantum by the solution always leads to the starting of a reaction chain, *i.e.*, if none of the light-absorbing molecules are again "deactivated" before they have time to react with oxygen, then we must expect the quantum yield to be a measure of the chain length. The fact that both our present work on the induced oxidation and my previous work on the rate of the photochemical reaction include measurements on benzyl alcohol-inhibited solutions, made under comparable experimental conditions, enables us to decide this point. My previous measurements, that were made in monochromatic light of wavelength  $254\mu\mu$  and of known absolute intensity, could be represented by a formula which, when applied to a solution containing 0.1 mole of benzyl alcohol per litre, gives a quantum yield of 64 molecules per  $h\nu$ . On the other hand, the data in Table I. show that the chain length at this alcohol concentration, which is well within the region where all the chains are broken by the inhibitor, is equal to  $28/0.48 = 58$  molecules. This is an agreement which can hardly be accidental.

As regards the photochemical reaction, we may express this result by saying that the induced, or "photosensitized," oxidation of the alcohol obeys the Einstein photochemical equivalence law. Exactly the same result was obtained by Cremer<sup>7</sup> in a study of a reaction to which I have referred earlier in this paper, *viz.* the photosensitized formation of water which accompanies the hydrogen-chlorine combination when oxygen is present.

Finally, we have also made some measurements on the copper-catalysed reaction which show that copper salts accelerate the total reaction without changing the ratio of sulphite oxidized to alcohol oxidized, *i.e.* without altering the chain length.

Summarizing the results of this investigation, it may be said that they seem to furnish a new and rather direct proof of the existence of thermal chain reactions; and that they throw some light on the mechanism by which reaction chains may be broken by an inhibitor.

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<sup>7</sup> Cremer, *Z. physik. Chem.*, 128, 285 (1927).

# THE INHIBITION OF CHAIN REACTIONS BY BROMINE.\*

By M. POLANYI.†

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## I. Chain Reactions Induced by Alkali Metal Vapour.

A sodium or potassium atom when brought into a mixture of  $\text{Cl}_2$  and  $\text{H}_2$  induces the formation of  $\text{HCl}$ , and from each alkali atom several thousand  $\text{HCl}$  molecules arise. The arrangement with which these induced chain reactions, as well as the analogous reactions described later, were carried out and examined is schematically shown in Fig. 1.

The hydrogen, under a pressure generally of 5-15 mm., circulates in the direction of the arrows shown at the entrance and exit of the pump.

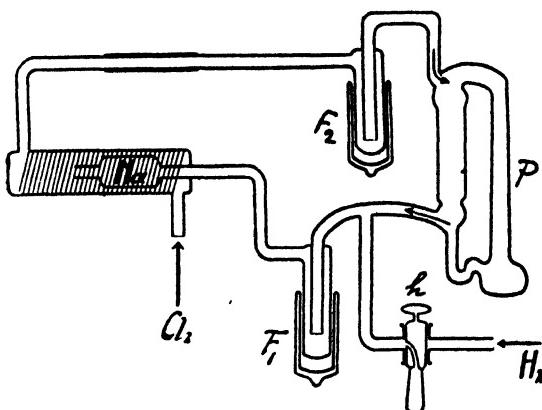
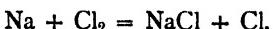


FIG. 1.—Scheme of Experimental Arrangement.

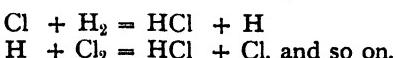
P = Mercury pump;  $F_1$ ,  $F_2$  = liquid air traps;  $h$  = inlet cock for  $\text{H}_2$ . One revolution introduces always the same quantity of  $\text{H}_2$ .

collected in the traps  $F_2$ . The hydrogen passes then again to the pump whence it is returned anew to the cycle. By means of the inlet cock  $h$  the quantity of  $\text{H}_2$  consumed is made up from time to time.

This phenomenon takes place according to the scheme whereby in the first place the alkali atom (*e.g.* Na) splits off an atom of chlorine,



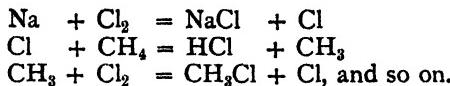
and thereafter a Nernst reaction chain follows,



\* Communication from the Kaiser-Wilhelm Institut für physikalische Chemie u. Elektrochemie, Berlin-Dahlem.

† This communication is an abstract of two papers which were written jointly with St. v. BOGDANDY and H. v. HARTEL. The first was published in *Z. Elektrochem.*, 33, 554, 1927, and the second is in proof in *Z. physikal. Chem.*

The inducing effect of alkali metal vapours can also be demonstrated in a mixture of  $\text{Cl}_2$  with a hydrocarbon. The halogen derivative of the hydrocarbon is thus formed, e.g.,



Such chains must under ideal conditions go on until the free atoms or radicles combine to form molecules. Many considerations however conduce to the premature end of the chain, probably because the free atoms or radicles react with impurities or unite at the walls of the chamber to form saturated molecules.

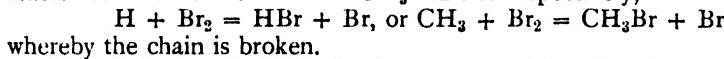
The effect of the wall is plainly shown in the following effects:—

- (1) The chain length (number of reactions in a chain) is shortened by reducing the partial pressure of the  $\text{H}_2$ .
- (2) Admixture with  $\text{N}_2$  increases the chain length.
- (3) The chain length is ten times as long if the wall is covered with a compact layer of  $\text{NaCl}$ .

## 2. Bromine Inhibition.

The phenomenon which we wish now more particularly to discuss is the arbitrary shortening of the chain length due to admixture of bromine. Other materials also exercise an inhibiting influence, e.g.  $\text{I}_2$ ,  $\text{HgCl}_2$ ,  $\text{HgBr}_2$ , etc., but for the present only the inhibition due to bromine has been sufficiently studied.

We conceive that bromine inhibition is due to the fact that the  $\text{Br}_2$  reacts with the free H atoms or  $\text{CH}_3$ -radicles respectively,



The chain length ( $K$ ) is, in the presence of bromine, inversely proportional, at a first approximation, to the proportion,  $a$ , of  $\text{Br}_2$  in the whole halogen concentration.

$$a = \frac{\text{Br}_2 \text{ conc.}}{\text{Cl}_2 \text{ conc.} + \text{Br}_2 \text{ conc.}}$$

If we call the proportionality factor  $\frac{2}{w}$  then

$$K = \frac{2}{aw} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $w$  gives the ratio of the velocity of the reaction of H with  $\text{Cl}_2$  to that of the reaction of H with  $\text{Br}_2$  (or  $\text{CH}_3$  with  $\text{Cl}_2$  to  $\text{CH}_3$  with  $\text{Br}_2$ ). We must have regard to the following corrections of equation (1):—

(1) With small concentrations of  $\text{Br}_2$  the fact that, even without addition of  $\text{Br}_2$ , there is a limit to the chain length, so that there is a certain natural inhibition, which markedly influences the chain length.

(2) With greater concentrations of  $\text{Br}_2$ , the fact that a part of the alkali metal becomes converted into alkali bromide and is thereby lost to the induced reaction.

Bearing in mind (1) and (2) we get the equation

$$K = \frac{2[(a + a_0)w + 1]}{(a + a_0)w(a + a_0 + 1)} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The correction  $a_0$  introduced here is calculated from the chain length measured in the absence of bromine,  $K_0$ , according to the formula  $a_0 = \frac{2}{K_0}$ .

The equation gives the chain length (depending on the quantity of bromine added) satisfactorily if  $w$ , for the  $H_2$  and  $Cl_2$  mixture is assumed to be 0.13 and for  $CH_3$  and  $Cl_2$  0.3. Hence a  $H$  atom reacts seven times more rapidly with  $Cl_2$  than with  $Br_2$ , and a  $CH_3$  radicle reacts thrice as rapidly with  $Cl_2$  as with  $Br_2$ .

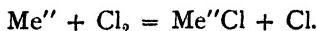
Variation of the temperature of the zone of the reaction shows that, in the case of the reaction induced between  $H_2 + Cl_2$ ,  $w$  diminishes slightly with increase of temperature (the inhibition decreases). This phenomenon is still obscure. Perhaps it is connected with the fact, which we have observed, that the thermal reaction between  $H_2$  and  $Cl_2$ , which sets in above 300° C. is catalysed by  $Br_2$ .

### 3. Induction by Divalent Metals and As, P.

We have now further examined whether the alkali metals can at all be replaced in their inductive effect by other metals or even metalloids. The result was positive. A series of divalent metals, Cd, Zn, Mg, as well as the metalloids As, P, gave an abundant inducing effect. At present only Zn and Cd (especially the latter) have been sufficiently studied, especially so far as concerns the above-described bromine inhibition, which is also found here.

### 4. Mechanism of the Reaction of Zn and Cd with $Cl_2$ .

The point which was of particular interest to us was whether we must consider in the case of the inductive effect of the divalent metals ( $Me''$ ) that  $Me''$  does not combine directly with  $Cl_2$  to give  $Me''Cl_2$ , but that it reacts according to the scheme



It might have been presumed that the inductive effect has its origin in a primarily formed activated  $Me''Cl_2^*$ , which latter either reacts with  $H_2$ , splitting off a hydrogen atom or collides with a  $Cl_2$  molecule and splits it up. If that were the case it might be expected that only a part of the added  $Me''$  atom would lead to the establishment of a chain, since a part of the primarily formed  $Me''Cl_2^*$  would lose its energy and thereby its reactivity, when colliding with a non-reactive molecule, before coming into contact with the partner of its reaction. In particular, if the chain-forming reaction consists in a splitting of  $Cl_2$  by  $Me''Cl_2^*$  an increase of the partial pressure of hydrogen would reduce the "inductive part" of the  $Me''$ ; if, on the other hand, it consists in a reaction of  $H_2$  with  $Me''Cl_2$ , an increase of the partial pressure of  $Cl_2$  would have this effect. In both cases admixture with inert gases such as  $N_2$  should reduce the "inductive part."

In accordance with these considerations we had to examine:—

(a) The proportion of the added  $Me''$  atoms which leads to the establishment of a chain (i.e. the "inductive part").

(b) If this part is smaller than 1, we have to establish how it depends on the partial pressure of  $H_2$  and of  $Cl_2$  as also on the pressure of added  $N_2$ .

The inductive part can be determined if we mix with the chlorine a known proportion of  $Br_2$ . From equation (2) we can then calculate the chain length and adjust for the total quantity of  $HCl$  (or  $CH_3Cl$ ) formed. Thus, for example,

$$\text{Number of inductive primary processes} = \frac{\text{Number of HCl molecules formed}}{\text{Chain length}}$$

and further,

$$\text{Inductive part} = \frac{\text{Number of reacting Me'' atoms}}{\text{Number of inductive initial processes}}.$$

The result of the measurement in the case of Zn was as follows: The inductive part was at pressures of 5-15 mm. H<sub>2</sub>, within experimental error, equal to unity. By admixture of N<sub>2</sub> (e.g. 10 mm. N<sub>2</sub> to 5 mm. H<sub>2</sub>) the inductive part was not diminished. Hence, in accordance with what has been said, we conclude that the primary process in this case does not consist in a formation of ZnCl<sub>2</sub>\* but takes place according to the formula



In the case of Cd the inductive part proved to be distinctly less than 1. A more close examination showed, however, that there was no primary formation of CdCl<sub>2</sub>\*, the real state of affairs being: The reaction Cd + Cl<sub>2</sub> = CdCl + Cl, with which the induction commences, proceeds much more slowly than the corresponding reaction Na + Cl<sub>2</sub> = NaCl + Cl and also more slowly than the reaction Zn + Cl<sub>2</sub> = ZnCl + Cl, so that a large part of the cadmium atoms reach the wall without reacting with Cl<sub>2</sub>; these atoms react along the wall without formation of chlorine atoms, since only the cadmium atoms which react in the gas phase have an inductive effect.

The dependence of the inductive part on the pressure of H<sub>2</sub>, and of Cl<sub>2</sub>, and on an admixture with N<sub>2</sub> affords verification of this view. It is clear that the inductive part varies proportionally with the number of collisions which the Cd atom suffers with Cl<sub>2</sub> in the course of its passage to the wall, etc.

(a) The inductive part increases (under constant partial pressure of Cl<sub>2</sub>) proportionally with the pressure of H<sub>2</sub>.

(b) It increases (under constant partial pressure of H<sub>2</sub>) proportionally with the pressure of Cl<sub>2</sub>. On admixture with N<sub>2</sub> it increases proportionally with the increase of the diffusion constant thereby effected.

This behaviour of Cd vapour towards Cl<sub>2</sub> suggests the conclusion, by chemical analogy, that the reaction Zn + Cl<sub>2</sub> = ZnCl + Cl does not (at any rate with any great degree of probability) take place like the reaction Na + Cl<sub>2</sub> = NaCl + Cl at each collision.

We have found, in fact, that by reducing by half the pressure of the hydrogen (to 2 mm.), in the case of Zn the inductive part becomes distinctly smaller than 1, and by addition of N<sub>2</sub> it can be raised again to 1. Zn behaves in the same way as Cd except that the reaction Zn + Cl<sub>2</sub> = ZnCl + Cl proceeds somewhat more rapidly than the corresponding reaction with Cd.

### 5. Velocity of the Reaction Me'' + Cl<sub>2</sub> = Me''Cl + Cl.

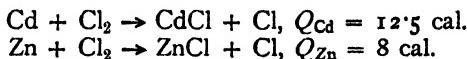
Since the metal vapour in our arrangement is led through a nozzle into the reaction chamber (and on account of the small pressure above-mentioned there is no turbulence) it must travel a certain distance by diffusion from the mouth of the nozzle to the wall if it is to reach the wall.

Now we can calculate from the diffusion constant the mean time which the metal atom needs to get to the wall, and on the other hand we can deduce from the partial pressure of the Cl<sub>2</sub> the number of collisions with Cl<sub>2</sub> which the metal atom will meet with during this time.

If we compare this number of collisions with the proportion of the metal which has an inductive effect, we find that it is likely that a collision of Me''

with  $\text{Cl}_2$  leads to the reaction  $\text{Me}''\text{Cl} + \text{Cl}$ . This calculation shows that each five-thousandth collision with chlorine gives rise to  $\text{ZnCl} + \text{Cl}$ , and in the case of Cd each hundred-thousandth leads to the analogous product  $\text{CdCl} + \text{Cl}$ .

Now the theory of reaction velocity states that the successful fraction of collisions is  $e^{-\frac{Q}{RT}}$ , where  $Q$  is the heat of activation. The above figures give



This leads to the further postulate that in the range in which the inductive part is less than 1 an increase of temperature in the reaction zone will raise the inductive part, according to the function  $e^{-\frac{Q}{RT}}$  when the values calculated above for  $Q$  are inserted.

In fact it appears, as much in the case of Cd as of Zn, that the induced reaction (with constant metal vapour supply) increases in extent considerably with increase of temperature if the conditions are so arranged that the inductive part is less than 1, and on the other hand, it is only slightly dependent on the temperature if the ratio is in the neighbourhood of 1. The figures which are obtained thus for the heat of activation are close to the above values calculated from the inductive ratio.

### 6. Heat of Formation of the Monochloride $\text{Me}''\text{Cl}$ .

Since the heat of activation of a reaction can never be less than the heat absorbed in the reaction, it follows that the reaction

$\text{Cd} + \text{Cl}_2 = \text{CdCl} + \text{Cl}$  consumes at the most 12.5 cal.  
and  $\text{Zn} + \text{Cl}_2 = \text{ZnCl} + \text{Cl}$  consumes at the most 8 cal.

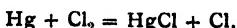
On the other hand, however, the heat of formation of  $\text{Cl}$ , from its atoms is 58.5 cal., whence it follows that the heat of formation of  $\text{CdCl}$  vapour from the atoms amounts to at least 71 cal. and that of  $\text{ZnCl}$  to at least 67.

If we suppose that here, as in other cases, the heat of activation in the reaction of atoms with molecules is equal to the reaction heat, these lower limits must be assumed to be equal to the reaction heat. It can indeed be shown that the reaction heat cannot be much higher than the heat of activation, since the divalency of Cd and Zn demands that the heat of formation of the monochloride from the atoms must be lower than half the heat of formation of the dichloride from the atoms. Therefore the heat of formation of  $\text{CdCl}$  from the atoms must be less than 75 cal. and that of  $\text{ZnCl}_2$  less than 78 cal.<sup>1</sup> We see that these upper limits for the heat of formation of the monochloride are not much higher than the lower limits given by the heat of activation. This confirms us in the conjecture that the heat of activation is in this case equal to the heat of reaction.

<sup>1</sup> This helps us to understand why Hg is unable to bring about inducing effects. The heat of formation of  $\text{HgCl}$  from the atoms is about 40 cal. Hence we calculate



At  $300^\circ \text{C}$ . each ( $e^{-\frac{18.5}{2.573}} = 10^{-7}$ )th collision leads to a combination



At such a small reaction velocity the Hg atoms must to an overwhelming degree reach the wall before they can react in the sens.:  $\text{Hg} + \text{Cl}_2 = \text{HgCl} + \text{Cl}$ .

### 7. Velocity of the Reaction $\text{Me}'' + \text{Cl}_2 = \text{Me}''\text{Cl}_2^*$ .

We have arrived at the definite opinion that Cd and Zn do not in general combine with chlorine to form the normal dichloride, but form a monochloride and a free chlorine atom.

From the figures given above for the collisions in the latter reaction we are able now to formulate this conclusion quantitatively, and to say that between Zn and  $\text{Cl}_2$  at least  $5 \times 10^{-3}$  collisions can take place without leading to the formation of dichloride, and that in the case of Cd this lower limit is about  $10^5$  collisions. Under given conditions approximately every  $10^5$  collision would be a three-body collision. Hence one sees that not every three-body collision leads to the formation of the dichloride.

### 8. The Effect of Bromine on the Thermal Reaction.

We also examined the question whether bromine inhibited the thermal formation of hydrogen chloride which sets in at about  $50^\circ$  above the temperature of experiment with induced reactions. The result was negative (as already mentioned) since bromine exercised not an inhibitive but a slightly accelerating effect.

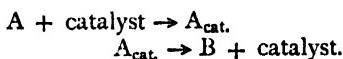
On the other hand, in the reaction between methane and chlorine there was a distinct inhibition of the thermal combination, and indeed to a degree equal with that in the case of the induced reaction. From this it follows that the thermal formation of hydrogen chloride does not bring about an atom chain; the thermal formation of methane chloride, on the other hand, follows a similar mechanism as the induced reaction between methane and chlorine.

## THE THEORY OF MOLECULAR DISLOCATION APPLIED TO HOMOGENEOUS CATALYSIS.

By J. BÖSEKEN.

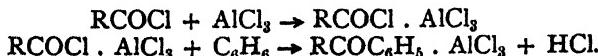
*Received 17th July, 1928.*

The most generally accepted explanation of catalytic phenomena in homogeneous solution, up till now, has been the intermediate products theory, which in the simplest case, isomeric change, can be symbolised as follows:—



As a result of my researches on Friedel and Craft's reaction, I pointed out as long ago as 1903 that in the most favourable case the theory at best explains the course of the reaction, but it can never explain *why* a catalyst accelerates a given reaction.<sup>1</sup>

From a study of the ketone synthesis it appeared that the  $\text{AlCl}_3$  very readily combined with the acid-chloride, forming a molecular compound, and that this substance reacted with the aromatic hydrocarbon, resulting in an  $\text{AlCl}_3$ -compound of the ketone:



<sup>1</sup> *Rec. Travaux Chim. P.-B.*, 23, 105, 1904; 24, 6, 1905; 29, 86, 1910, etc.

This seemed to give a complete explanation of the reaction, both as to the course of the synthesis and as to the action of the  $\text{AlCl}_3$ , whereby the acid-chloride compound becomes accessible to the benzene.

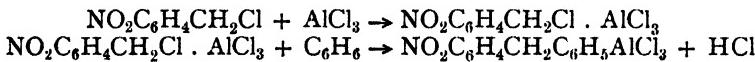
A closer study of this and of other cases, however, soon made it clear that this explanation could not be correct. Firstly, a great number of substances such as  $\text{CHCl}_3$ ,  $\text{CCl}_4$ , sulphur, ethylene, ethyl chloride and many others were found, which have no greater tendency than benzene itself to form addition compounds with  $\text{AlCl}_3$  and yet, as is well known, underwent the reaction very readily. On the other hand, such a substance as  $\text{POCl}_3$  yielded a beautifully crystallised addition-product, which can be crystallised from benzene without attacking it.

These examples clearly show that the mere formation of addition-products cannot serve as an explanation of the catalytic action. Another example may make this even clearer: Benzyl chloride does not combine with  $\text{AlCl}_3$  to form a molecular compound, but it is resinified with formation of hydrochloric acid.

The three isomeric nitrobenzyl chlorides form well-crystallised addition-products; it may be assumed that the  $\text{AlCl}_3$  is bound to the nitro-group, since nitrobenzene also unites with  $\text{AlCl}_3$ . And yet, benzyl chloride undergoes the Friedel and Craft's reaction even with traces of  $\text{AlCl}_3$ , whereas the nitro derivatives need at least one molecule  $\text{AlCl}_3$  and even then the reaction progresses much more slowly.

From this we may conclude that the catalyst works best when it is least firmly bound, and that the C—Cl bond must be activated in these substances; it is clear also that, when the  $\text{AlCl}_3$  is attached to the nitro group, it is prevented from carrying out this activating action.

This reaction may be represented by the scheme:—



which appears to be correct in form, but is actually misleading.

In the same way it is evident that in the compounds of  $\text{AlCl}_3$  with acid-chlorides the catalyst is attached to the CO-group and that the ketone synthesis does not take place because of the existence of this bond, but, rather, despite its existence, the catalyst may be considered as partially paralysed. Hence the above scheme, if applied to ketone synthesis, is again misleading. It may be correct in form, but it gives no indication of the real course of the reaction and the question as to why the catalyst activates the C—Cl— bond and the benzene remains unsolved.

The Friedel and Craft's reaction is usually far too intricate to make it possible to separate the strictly catalytic from the other phenomena. This separation will be simpler with the more elementary transformations, e.g. with the allotropic change of one element under the catalytic influence of another.

For this purpose I choose the change of white phosphorus into red under the influence of iodine. In this case, at low temperatures, the compound  $\text{PI}_3$  or  $\text{P}_2\text{I}_4$  arises; if this substance is heated it breaks up into iodine and red phosphorus.

The most obvious assumption is that there is a succession of reactions by way of intermediate products, since this change occurs also at  $200^\circ$ , in which case the formation of iodine is no longer to be perceived, but, immediately after the introduction of the iodine vapour into the molten white phosphorus, red phosphorus appears.

This, however, can by no means be called an explanation of the action

of iodine, as the catalysis proper takes place either before the formation of the phosphorus-iodide or after its decomposition. Since at low temperatures, *e.g.* 100°, the experiment shows formation of  $\text{PI}_3$ , I will assume that there are two ways in which the transformation from white to red phosphorus occurs.

(1) The first method, which I will provisionally call the pseudo-catalytic, is the one sketched above, *viz.*, the formation firstly of the iodide followed by its decomposition.

(2) The second method, the more purely catalytic one, is the transition of the white phosphorus, in contact with  $\text{I}_2$ , to a labile condition in which it can pass into stable red phosphorus.

It happens, by chance, that we can in this case form a clear idea of these two methods, because the white phosphorus molecule consists of four atoms, whereas in the iodides there are only one or two atoms. In the first method the white phosphorus molecule must be broken up before this compound is formed. This is not necessary when the reaction proceeds in the second way: the  $\text{P}_4$  molecule may have passed into an isomer or into another state of energy, which amounts to the same thing.

The second method for white phosphorus to pass into red is much simpler. This change of state of the  $\text{P}_4$  molecule is necessary, but at the same time also sufficient. The fact that red phosphorus is obtained in the pseudo-catalytic cycle is certainly due not to the formation of  $\text{PI}_3$  or  $\text{P}_2\text{I}_4$ , but to the circumstance that this compound is decomposed pretty easily, during which process the phosphorus also is separated in an active form, which need not be identical with the active form of the direct method, but which also causes it to pass into the red state, which latter again need not be identical with the red phosphorus obtained by the indirect method.

If we take another catalyst, *e.g.*  $\text{AlCl}_3$ , which does not combine with phosphorus, then again a transition takes place—this time into a yellowish orange modification—and when at the same time benzene is present, it takes place very quickly. In this case there is therefore no question of a compound like that of  $\text{PI}_3$ , and yet the bonds of the  $\text{P}_4$  molecule are activated in such a way as to give the phosphorus an opportunity of passing into a stabler state; so the primary change of state of the white phosphorus is of chief importance.

A similar catalytic phenomenon takes place with the incomplete combustion of white phosphorus, in which part of the  $\text{P}_4$  molecules passes into the red state, as the so-called phosphorus suboxide is nothing but a modification of the red phosphor which has inclosed phosphorus oxide.

I think that this example most clearly illustrates the two classes of catalytic phenomena and that in all cases the stress must be laid on the change of the activity of the molecule in consequence of the meeting with the catalyst. This process, which is physical rather than chemical, might therefore be called *physical catalysis*, to distinguish it from the process which obviously leads to intermediate products and which might be denoted *chemical catalysis*, remembering that in this case, also, the change of state of the molecule (*i.e.* the physical part) is of paramount importance.

We can here even go a step further and with reference to the phenomena mentioned with regard to the Friedel and Craft's reaction express the conviction that the chemical process, the formation of intermediate compounds in consequence of the fixing both of the molecule and of the catalyst, hampers the reaction.

Other chemists too have felt this contradiction and they therefore seek for an explanation in the reactions which lead to the intermediate products

rather than in the formation of these products. I go a step further and consider the change of state of the molecules during the collision with the catalyst as of chief importance. To this change of activity of the molecule I have given the name of dislocation or disruption; it takes place immediately and can be compared as regards its rapidity with an ion-reaction and is therefore undoubtedly electrical in nature.

Similarly we may assume that the action of the H-ions and of the acids during esterification and saponification is due to a shifting of the electric field between the oxygen and the hydrogen of the alcohol (or of the water) and of the double bond of the oxygen of the CO-group of the acids (or of the esters).

An important quantitative difference between chemical and physical catalysis is caused by the different period of adhesion, the time during which the molecule to be activated and the catalyst stick together (the "sticking-time"). In the case of physical catalysis the meeting has more of the character of an elastic collision than in the case of chemical catalysis. This difference probably amounts to a discontinuity; consequently the kinetic and thermodynamic relations are also different and we must consider them separately.

In the case of physical catalysis an isomeric change, as sketched above, is in the simplest case a bimolecular reaction, but in the case of chemical catalysis it is a succession of bimolecular and monomolecular reactions.

We should not forget that the most important part of the process takes place either during the collision or during the adhesion. This occurs accordingly within the period of the elastic collision in the first case and at the beginning or at the end of the adhesion in the second case; that is to say, the most important event will be hidden from kinetic observation, as the period of an elastic collision is of the order of  $1 \times 10^{-12}$  second.

I will give another simple example to elucidate the notion of dislocation, at the same time availing myself of the opportunity to throw light upon the specific action of the catalyst.

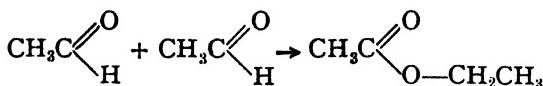
Acetaldehyde is polymerised in *four* directions:

- A: into paraldehyde (trimere) and metaldehyde (hexamere).
- B: into aldol:  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO}$ .
- C: into ethylacetate:  $\text{CH}_3\text{COOCH}_2\text{CH}_3$ .
- D: into dimethylglycolaldehyde:  $\text{CH}_3\text{CHOHCOCH}_3$ .

The first reaction takes place under the influence of acids  $\text{H}_2\text{SO}_4$ ,  $\text{ZnCl}_2$ ,  $\text{HCl}$ , etc.; it is clear that these acids influence the unsaturated oxygen and change it into the state of oxonium; in connection with this only the  $\text{C}=\text{O}$  bond is activated and the polymer acquires the structure of an ether and is not attacked by alkalis. Here too we feel that the formation of the oxonium salt or even of the cation cannot be essential, but that the first stage, which can be represented by a shifting of electrons, is the determining factor.

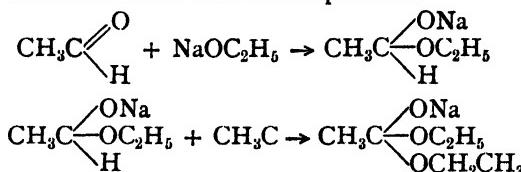
In polymerisations B and C, one of the H-atoms, either of the methyl group or of the aldehyde group, plays an important part: as these H-activations are in essence acidifications, it is to be expected that they will be furthered by alkalis or substances of an alkaline character. This is especially the case with the aldol polymerisation, where an H of the  $\text{CH}_3$  group must be activated and the molecule will be dislocated in the direction of the enol. In the case of pseudo-catalysis the enol may act as an intermediate product in the form of the anion, but we feel again that the formation of this negatively-charged ion is not essential.

In the third polymerisation (C) the formation of an ester where the shifting of the aldehyde-hydrogen atom from one molecule to the unsaturated carbon atom of the other :



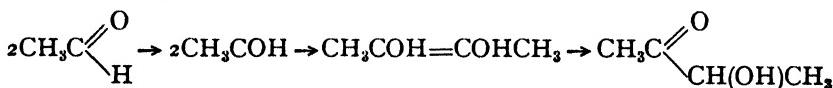
is the point at issue, alkaline substances will likewise be the best catalysts, and in connection with the formation of esters alcoholates are called for.

Here, too, the formation of an addition-product :



which might be assumed with the chemical catalysis, is not essential. When we take aqueous alkalis we get again the aldol-reaction or Cannizarro's reaction, which is thus explained.

Lastly the fourth reaction, the formation of dimethylglycolaldehyde, plays an important part in biology ; it is analogous to the former ; the aldehyde-H-atom is activated, but this H now goes to the unsaturated oxygen-atom of the other molecule :



It is therefore to be expected that this reaction will take place in aqueous solutions and under amphoteric conditions, in consequence of which it becomes biologically possible. It has not yet been realised in the laboratory without micro-organisms ; we may expect that it can take place on the surface of amphoteric elements, and we feel how eminently important it is to carry out this reaction, but, alas, amphoteric elements show very little activity.

From this example we see that the catalysis of one and the same substance under the influence of different catalysts proceeds in quite different ways and we think we have demonstrated that each of these kinds gives rise to a special dislocation when meeting with an aldehyde-molecule. The aldehyde-molecules thus activated will differ from each other in all respects, and at the collisions with similar molecules must therefore give totally different polymerisation products.

It is perhaps not unimportant to point out the catalytic polymerisation of benzaldehyde. This aldehyde has a more or less acid character, and therefore I presume that the formation of a polymer of the character of paraldehyde is not possible. Of course, the aldol-condensation does not take place in this case, because the H-atom essential to this is wanting. There remain the ester and the benzoin polymerisations, which in this case, in consequence of the acid reaction of the aldehyde, are both brought about by specific more or less alkaline catalysts.

Finally, chloral occupies a very special place, as it forms a polymer, both with acid and with weakly alkaline catalysts, which undoubtedly differs from any of those treated before, since it is amorphous and, in contrast with paraldehyde and metaldehyde, is sensitive to alkalis ; by strong alkalis it is decomposed, like aldehyde itself, into formic acid and chloroform.

Consequently the question arises : How are we to visualise the dislocation ? When we examine the molecules in general we are struck with the fact that a number of them, notwithstanding great affinities, have little or no influence on each other. These are often molecules consisting of two or more atoms and it is assumed that these atoms are so closely in contact that their electric field is shut off : the so-called non-polar bond. They might be compared with well anchored electro-magnets or toroids. Catalysts on the contrary are often ions, or molecules of one atom, or, if they consist of more atoms, are molecules of a peculiar character with an open power-field with polar bonds.

Hence I see the dislocating action of catalysts in the fact that they are able to communicate this open polar character by means akin to induction, that is to say very quickly, to the closed systems, so that these latter are in a more polar condition either during the elastic collision or during the adhesion (see above).

From this conception it can be easily understood that a catalyst can attach itself so closely to one of the molecules as to form a new non-polar system ; the catalyst is bound too closely : it is inhibited.

Negative catalyses also can be considered from this general point of view, since *a priori* it is as probable that a polar molecule should change another molecule into a state of greater polarity as that a polar system should pass by means of a second substance into a less polar system. Thus I see in the action of the so-called anti-oxygens a mutual removal of the polarity with regard to the molecular oxygen. The way in which this paralysis takes place must be verified in each particular case by kinetic investigation.

I desire to draw attention to a research by Reinders and Dingemans, who have found that sodium sulphite strongly retards the oxidation of hydroquinol, it being proved at the same time that the sulphite was oxidised. So it seems as if the electric field of the quinol which was accessible to the oxygen is shifted on to the sulphite, to which we may add that the hydroquinol also exercises a protective action on the oxidation of the sulphite which must be attributed to the fixation of a positive catalyst (in this case cupric ions). So the sulphite acts as an electric conductor, for which again the formation of an addition-product between hydroquinol and sulphite cannot serve as an explanation, since it would not then be clear why *one* molecule of sulphite can protect a great number of molecules of hydroquinol. The cluster theory together with the dislocation theory probably gives an explanation.

Before entering into a somewhat more detailed examination of the nature of dislocation, I will consider for a moment the question whether in bimolecular reactions—with which one has usually to deal in practice—the catalyst causes dislocation in one or in both molecules. From what has been said before it follows that the activity is obvious on both molecules. The electric field of one of the molecules is opened to make it accessible to the other ; but the latter must, at the appropriate place, be attracted by the changed field ; hence that place must be likewise activated. With the Friedel and Craft's reaction, not only a definite bond of the *one* molecule, but also the CH-bond of the benzene must be activated. With the acetylation of alcohols and amines, both the acetic anhydride and the NH- or OH-bond must be dislocated ; consequently, pyridine as an acetylating catalyst is excellent for phenols, but absolutely powerless for diphenylamine, because although it dislocates the (acid) phenolic hydrogen, it has no effect on the (basic) NH-bond.

In choosing catalysts this should be thoroughly considered ; metals,

e.g., will be hydrogenation catalysts of unsaturated substances, because they activate both the hydrogen molecule and the double bond; on the other hand, metallic oxides of a weakly acid nature, such as  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , etc., are hydration catalysers and metallic oxides of a weakly basic nature, such as  $\text{MnO}$  and  $\text{ThO}_2$ , activators for the separation of  $\text{CO}_2$  from the fatty acids.

In order to obtain an idea of the nature of these dislocations I have been for several years, in collaboration with W. D. Cohen, Muller, and S. L. Langedijk, engaged in the examination of some photo-catalytic phenomena, namely the photo-oxidation of primary and secondary alcohols under the influence of certain ketones.<sup>2</sup>

From the investigations of Ciamician and Silber it was known that, when an alcoholic solution of benzophenone is exposed, this mixture passes into benzpinacone and aldehyde. If a sufficient amount of oxygen is present, the ketone remains seemingly unchanged and the alcohol is oxidised into aldehyde and water; it has then become a photo-catalytic process. The aromatic ketones appear to absorb the active light; so it may be said that by the absorption of light the benzophenone passes into an active state; this state disappears as soon as the exposure has ceased, presumably at once, but at all events after an extremely short time.

So what really happens is that the benzophenone has passed into an isomer which, on account of the manner in which it has arisen, may be called a photo-isomer. If now the molecules of this isomer collide with alcohol molecules, then two of its H atoms are activated, which either affect the ketone or, if oxygen is present, form water with them. Consequently the closed, weakly polar benzophenone passes into a more strongly polar state. If alcohol molecules collide with this, the two typical H-atoms by a kind of induction also become polar and so active that either they reduce the ketone or are quickly oxidised by oxygen.

So this process is a secondary dislocation of the alcohol. We can see these dislocations in some cases, because the compounds of some alcohols and ketones are, when exposed, of a vivid yellow colour.

When we studied this reaction kinetically, it proved to proceed in such a way that two molecules of ketone acted on one molecule of alcohol; thus it is as if the alcohol-molecule inserts itself between two poles, *viz.*, the dislocated  $\text{C}=\text{O}$ -groups of the benzophenone molecules, where it is then itself immediately activated and then quickly attacked.

An investigation in the physical laboratory at Leyden has made it appear probable that during the exposure of benzophenone in the photo-active section of the spectrum no electrons are emitted; so the activating does not pass into ionisation, the increase of energy being insufficient, yet apparently large enough to cause the reactions observed to take place with great velocity.

At a common catalysis, exposure, *i.e.* energising from without, is not necessary; the catalyst is in itself able to make the molecules colliding with it undergo a sudden change of energy, which, with the so-called monomolecular reactions, gives rise to isomeric changes or decompositions, and with the polymolecular reactions enables the molecule to enter into reciprocal action with equal or different molecules.

Dislocation is nothing but a change of energy, and as this naturally belongs to the sphere of physical chemistry, it goes without saying that attempts have more than once been made to shed light on catalytic actions from a thermodynamic point of view.

<sup>2</sup> Rec. Travaux Chim. P.-B., 39, 261, 1920; 40, 433, 1921; 46, 303 and 717, 1927.

The most rational way was to start from ordinary chemical reversible reactions and then to try and place the catalytic reactions in this category. The most important step was taken long ago (1889) by Arrhenius. As the enormous acceleration of almost all reactions on raising the temperature cannot be accounted for by the simple increase of the number of collisions. (because for 10° C. this would only amount to an increase of a few percents.), Arrhenius assumed that only a very small number of molecules is sufficiently active to react and that this number is increased by rise of the temperature. The relation between the reaction-constant and the temperature becomes according to him (integrated)

$$\ln K = - \frac{A}{RT} + B,$$

in which  $A$  indicates a difference of energy, *viz.*, the difference of energy between the active molecules and the average energy of the whole mass.

Since then the meaning of the magnitude  $A$  has scarcely changed, but that of  $B$  remained indefinite till 1911. Then Scheffer and Kohnstamm<sup>3</sup> assumed, basing their assumption partly on the classic laws of thermodynamics, partly on kinetic considerations, that in order to be able to react the molecules had to go through a particular state, *the intermediate state*, characterised by a definite difference of energy with regard to average energy and by a definite difference of entropy with regard to average entropy (both on the supposition that the concentration = 1). By this they arrived at a more definite meaning of the magnitude  $B$  of Arrhenius. The formula of Arrhenius-Scheffer-Kohnstamm runs as follows:—

$$\ln K = - \frac{\Sigma_i - \Sigma_m}{RT} + \frac{\eta_i - \eta_m}{R} + C,$$

in which therefore  $\Sigma_i - \Sigma_m$  respectively  $\eta_i - \eta_m$  ( $C = 1$ ) represent the differences of energy and entropy in question.

Arrhenius assumed that a positive catalyst made the difference of energy,  $A$ , smaller, and that consequently,  $\ln K$  became greater. This supposition, *a priori* rational, involves however, in connection with the original formula of Arrhenius:  $\frac{d \ln K}{dT} = \frac{A}{RT^2}$  that the temperature-coefficient in the presence of a catalyst must always be smaller than without the catalyst ( $A$  is negative).

Now this was proved by the experiment to be untenable, as by investigations referring to this matter this coefficient was found to be greater.<sup>4</sup> All theories which did not account for the real meaning of  $B$  failed on this account.

Scheffer's formula alone gives a satisfactory explanation of these facts. With a positively catalysed reaction  $A$  can become greater, provided that the difference of entropy has considerably increased.

If in the simplest case, the physical catalysis of an isomeric change, we apply the formula of Scheffer, whether in the presence of a catalyst or not,

$$\ln K = - \frac{\Sigma_i - \Sigma_m}{RT} + \frac{\eta_i - \eta_m}{R} + C \text{ (without catalyst)}$$

$$\ln K' = - \frac{\Sigma'_i - \Sigma_m - \Sigma_{\text{cat.}}}{RT} + \frac{\eta'_i - \eta_m - \eta_{\text{cat.}}}{R} + C' \text{ (with catalyst),}$$

<sup>3</sup> Proc. R. Acad. Amsterdam, 13, 789 and 15, 1109.

we see that the energy and the entropy of the intermediate state are altered by the catalyst, which follows since in this intermediate state both the molecule and the catalyser are present.

In a bimolecular physical catalysis both the molecules together with the catalyst attain the intermediate state at the same moment; that is to say, dislocation takes place in one as well as in the other molecule. So we see that the state of affairs assumed in our general examination as self-evident, and also supported by the experiment, follows also from the thermodynamic deduction of Scheffer.

All molecules which take part in a reaction undergo a change. *A priori* there is not much to be said as to the amount and the sign of these alterations; it may, however, be assumed that with physical catalysis these amounts with regard to the *energy* will be small and will decrease in proportion as we approach to the ideal catalysis.

When, on the other hand, we have to deal with a chemical catalysis, we cannot apply the above-mentioned simple formulæ, as chemical catalysis is a succession of at least two reactions.

If, to avoid too much detail, we include these in one formula as above, then the differences of energy in the catalysed reaction will no doubt be quite different from those in the reaction without a catalyst, and this has indeed been found by Van Thiel in a concrete case.<sup>4</sup>

To put this in a very simple form we may argue as follows: In physical catalysis, where only small shifting of energy are to be considered, we may expect that the energy of activation does not greatly change and so the change of velocity will be governed by the differences of entropy, that is to say the chance of a favourable collision is almost exclusively defined by factors of a steric nature, among which I include the enlargement of the polar sphere. If we use the idea of the well-anchored magnet, we can suppose that the pushing away of the anchor does not take much energy, while the outside effect may be very great.

On the other hand, with chemical catalysis the differences of energy will also be considerably altered and in my opinion always in a positive sense, that is to say, in consequence of the formation of an intermediate product more energy will be required to give to the molecules the necessary reaction-energy. As we saw above, this in itself ought to produce a slower reaction; to ensure a quicker reaction the differences of entropy must consequently increase much more strongly; so the factors of a steric nature considered above must, for a more favourable collision, be altered even more considerably than in physical catalysis.

Scheffer has expressed the result of Van Thiel's investigation very graphically as follows: the mountain that has to be crossed has been made higher by the catalyst, but the pass has become broader and smoother.

It is evident that experiment is needed to confirm the above-expressed supposition, that in physical catalysis the *A* term of Arrhenius remains all but unchanged and the *B* term is enlarged, whereas in chemical catalysis the *A* term *always* increases. A large field of study lies open, it being in the first place necessary to settle whether the separation between physical and chemical catalysis is effective. Now, it is certainly remarkable that in heterogeneous catalysis such a case has been discovered by Scheffer and his collaborators. When studying the methane-equilibrium under the influence of metallic nickel this reaction proved to be one of physical catalysis above 420°, that is to say, this metal did not form a stable com-

<sup>4</sup> E. v. Thiel, *Thesis, Delft, 1922*, and *Proc. R Acad., Amsterdam*, **25**, 210, 1922.

bination either with carbon or with hydrogen or with methane. Below  $420^{\circ}$  the position became quite different, the nickel forming a carbide with carbon, this compound being then reduced to methane and nickel by the hydrogen.

With this heterogeneous equilibrium with three solid components a sudden change is to be expected. From the foregoing considerations it becomes clear that above  $420^{\circ}$  a simultaneous dislocation of Ni, C and H<sub>2</sub> (intermediate state of Scheffer) takes place, and as this is an equilibrium reaction, this intermediate state is identical to that which arises between the Ni and the methane under the same circumstances.

Below  $420^{\circ}$  the process is pseudo-catalytic and consequently much more intricate. Yet we must imagine that in the nickel-carbide the carbon bonds, though attached to the nickel, have become more accessible to the hydrogen molecule (equally dislocated by the nickel) than they were without that metal.

*Technischer Hochschule,  
Delft.*

## A NEW CASE OF PHOTO-CHEMICAL CATALYSIS. THE REACTION BETWEEN NITRIC OXIDE AND CYANOGEN AND ITS MECHANISM.

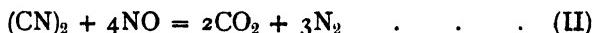
By R. G. W. NORRISH AND F. F. P. SMITH.

*Received 24th September, 1928.*

In an investigation of the photochemical properties of cyanogen it was found that the system cyanogen-nitric oxide yields an interesting result when illuminated by light of wave length shorter than  $360\mu\mu$ , furnished by an air cooled mercury vapour lamp. No reaction occurs in the dark, nor when the reactants are illuminated separately, save a very slow polymerisation of cyanogen, but when a mixture of the two gases, each at a partial pressure of  $\frac{1}{2}$  to  $\frac{1}{3}$  atmosphere, is exposed a number of changes take place, the net result of which may be represented by the equation



The cyanogen thus plays the part of a photochemical catalyst, but is itself slowly removed by a secondary reaction whose final result is represented by the equation



The above changes, however, fail to occur unless a trace of oxygen be added to the system; this is usually present in normal working, but by using pure reagents and complete evacuation, the reaction can be suspended at will, until a trace of oxygen is admitted. The oxygen may thus be said to play the part of a catalytic promoter to the cyanogen.

The equations given above represent only the end products of the reaction; the intermediate changes during the illumination lead to the conclusion that an intermediate compound of considerable stability between the nitric oxide and cyanogen is produced. This compound is believed to be the hitherto unknown nitrosyl cyanide NOCN. It decomposes spontaneously in the dark to give nitrogen, oxygen and cyanogen, the

change extending over several days, as will be seen by a consideration of the experimental facts set out below.

### Experimental.

The reaction chamber (Fig. 1) consisted of a double-jacketed cylindrical quartz vessel made in one piece, of 124 c.c. capacity, connected to the apparatus by a ground glass joint. It was kept at 25° C. by a stream of water pumped from a thermostat. The system could be evacuated by means of a water pump and a Toepler pump, the pressure being indicated by a vertical mercury manometer which could be isolated by a stop-cock when dealing with corrosive gases. The pressure in the system, and also small pressure-changes during reaction, could be measured by means of a Bourdon gauge, as used by Norrish.<sup>1</sup>

The cyanogen, prepared by heating mercuric cyanide in an electric furnace, and dried by passage over phosphoric oxide, was condensed and stored in a liquid air trap attached directly to the apparatus. The nitric oxide was obtained by treating ferrous sulphate and sulphuric acid with sodium nitrite solution, after the method of Thiele.<sup>2</sup> It was collected and stored in an aspirator over caustic soda, and could be introduced into the apparatus through a drying tube of phosphoric oxide.

The reaction vessel was illuminated by a mercury vapour lamp placed parallel at a distance of two inches, and could be screened from the light by a vertical brass plate actuated by hand. The lamp was run from storage batteries at 220 volts and consumed a current of 4 amps. with a potential drop of 150 volts across its electrodes.

For analysis of the products a gas pipette of special form was attached by capillary tubing to the apparatus (Fig. 2). It consisted of a bulb A of about

250 c.c. capacity terminated by a graduated tube B of about 50 c.c. capacity. The bulb was connected to a mercury reservoir C, and to the apparatus via a stop-cock D. The top of the graduated tube was also connected with absorption bulbs FF via stopcock G. In carrying out an analysis the pipette was completely evacuated by connecting through the apparatus with the pumps, the mercury reservoir being lowered; the products of the reaction were then expanded from the reaction chamber to the pipette. The mercury in the reservoir was then raised and the volume of gas measured in the graduated cylinder at atmospheric pressure. The gas was then transferred to the absorption bulbs where it was subjected to the action of the necessary absorbing agents, in the usual way. By this means it was found possible to make a satisfactory analysis of the products of the

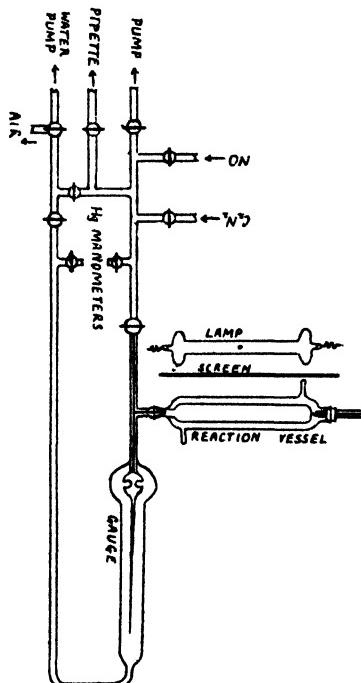


FIG. 1.

reaction, and with an accurate knowledge of the relative volumes of the pipette and reaction vessel, to obtain their actual pressures at the end of the reaction.

In order to carry out an experiment, the reaction vessel and gauge were evacuated, first by the water pump and later by the Toepler pump, and the nitric oxide and cyanogen were introduced from their separate containers by way of controlling stopcocks. The stopcock closing the reaction vessel and gauge was then closed. The partial pressure of each gas used was  $\frac{1}{2}$  to  $\frac{1}{3}$  atmosphere, and was accurately measured by the Bourdon gauge. The lamp was started, the screen remaining closed, and the system observed in the dark for an hour or more while the lamp reached a steady state of burning. During this period no change of pressure occurred; the screen was then raised and the following changes occurred:

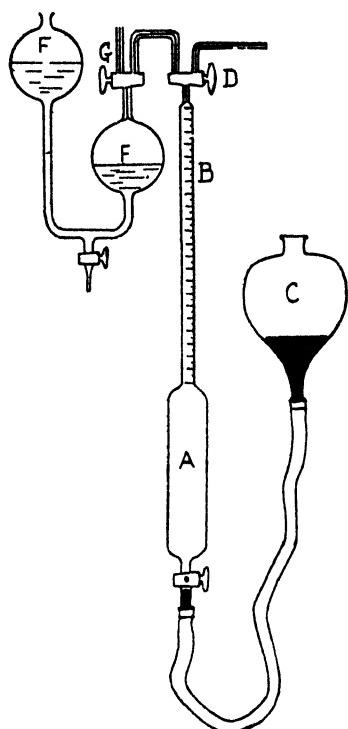


FIG. -2.

(a) A perfectly reversible, instantaneous "Draper" effect gradually developed and reached a limiting value of 8 to 13 mm. Hg after 20 hours' illumination. Thus upon sudden screening there was an immediate fall of pressure, which was reversed on re-illumination. Curves showing the development of this "Draper" effect are shown in Fig. 3. The effect is similar to that observed in the photochemical reaction between hydrogen and chlorine and is probably indicative of the onset of an exothermic photo-chemical reaction.

(b) The initially colourless reaction mixture gradually developed a yellowish tinge, and after prolonged illumination the colour became quite brown.

(c) At the same time a fall in pressure occurred, the rate decreasing with time, until an equilibrium pressure was reached after 20 to 40 hours' illumination. Examples are shown in Fig. 4.

(d) If illumination was interrupted, for instance, overnight, a fall of pressure always occurred, showing that some dark change was occurring in the system: this change was often accompanied by a small increase in the "Draper" effect. This dark pressure fall is indicated by the breaks in the curves of Fig. 4.

(e) In certain cases none of the above effects could be obtained, and the system remained unchanged under illumination until a trace of oxygen (about 1 mm.) was admitted when the normal effects gradually developed. This effect is shown particularly in curve (I) in Fig. 3, and in curve (II) whose form suggests an autocatalytic process, depending on the development of oxygen and therefore of nitrogen peroxide in the system. The inference is consequently drawn that in the cases where the reaction started spontaneously some oxygen was already present as an impurity, and the curves all take the same shape if produced back in the form suggested by curve (II) to a point representing zero oxygen content. The initial low sensitivity of

the mixture represented by curve (II) is also seen in the corresponding curve (II), Fig. 4.

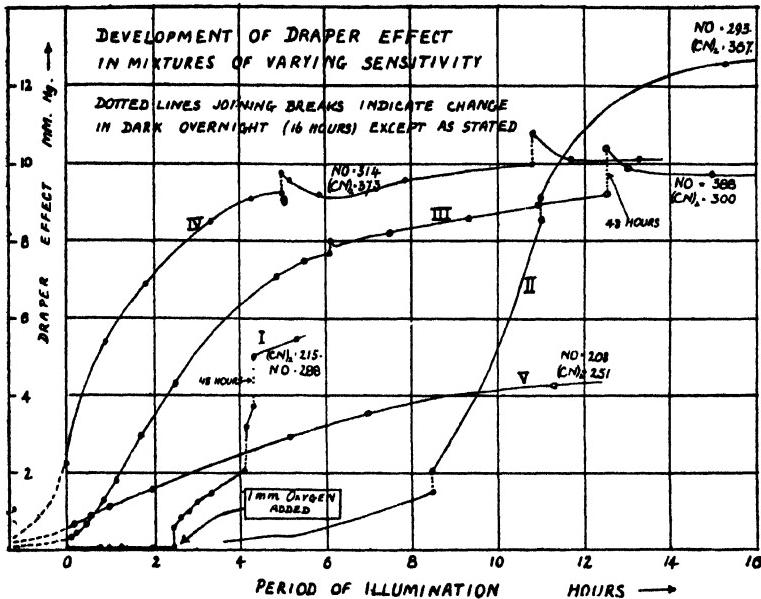


FIG. 3.

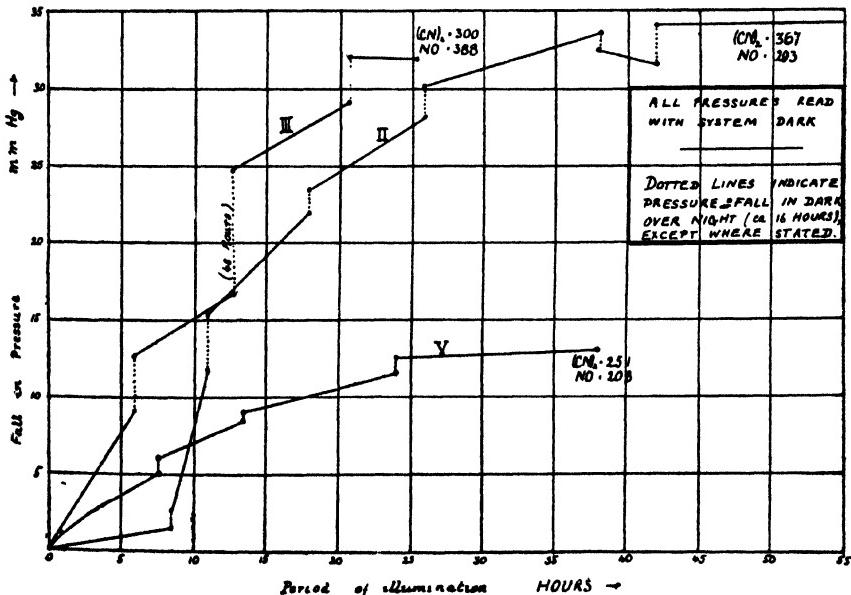


FIG. 4.

(f) If a sheet of glass were interposed between the reaction vessel and the lamp, none of the phenomena described above were observed. The wave-length of the active light must therefore lie in the region  $360-220 \mu\mu$ .

since the glass transmitted light of wave-length longer than  $360 \mu\mu$ , and the lamp furnished no light of shorter wave-length than  $220 \mu\mu$ .

(g) The following gases were found to accumulate as a result of the reaction :—

1. Nitrogen peroxide,
2. Nitrogen,
3. Carbon dioxide,

there remained also, unchanged nitric oxide and cyanogen.

These gases were detected in the following ways :—

*Nitrogen Peroxide*.—When the contents of the reaction vessel were evacuated through a trap cooled with solid carbon dioxide and ether, a solid blue deposit collected, suggesting dinitrogen trioxide. This deposit warmed up to give a brown gas, which on readmission to the reaction chamber, behaved photochemically exactly like nitrogen peroxide, giving the increase of equilibrium pressure described by Norrish.<sup>3</sup> The brown gas was next withdrawn into a tube with two plane ends and examined in a spectro-photometer when it gave the absorption spectrum of nitrogen peroxide. It also attacked mercury and did not obey the gas laws when cooled to  $1^\circ \text{C}$ ., giving a pressure lower than that to be expected.

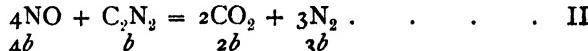
*Carbon Dioxide*.—After evacuation through the mixture of solid carbon dioxide and ether, the gas which passed on consisted mainly of nitric oxide. It gave a white precipitate with baryta water, and the solution failed to yield the Prussian blue test for cyanides. The cyanogen was therefore all retained in the trap, and carbon dioxide was present among the products of reaction.

*Nitric Oxide* was detected and measured by absorption in saturated ferrous sulphate solution; 10 or 12 hours were necessary for complete absorption.

*Nitrogen* was detected as an inert non-absorbable gas remaining after the contents of the reaction vessel had been treated with soda to remove cyanogen, nitrogen peroxide, and carbon dioxide, and with ferrous sulphate solution to remove nitric oxide.

Tests for carbon monoxide were made with ammoniacal cuprous chloride, but on no occasion was any detected.

Carbon dioxide, nitrogen peroxide and nitrogen being the only end products of the reaction, we are confined to the two equations—



The observed fall in pressure is due to the first reaction, while carbon dioxide accumulates as a result of the second. It will be observed that the first reaction is a purely catalytic process, in which cyanogen plays the part of catalyst.

The validity of these equations was tested as follows :—

The reaction was allowed to proceed, for several days, both in the light and dark. During this period a continued decrease of pressure occurred, but the decrease during illumination tended to zero as the reaction proceeded. This is shown in Table I.

TABLE I.

Pressure of cyanogen = 304.5 mm.  
Pressure of nitric oxide = 449 mm.

Period of Observation.	Condition of System.	Fall of Pressure mm.
6½ hrs.	Light	11.5
16 " (overnight)	Dark	9.5
4 "	Light	2.5
16 " (overnight)	Dark	6.5
5½ "	Light	2.5
16 " (overnight)	Dark	5
3½ "	Light	0.5
48 " (week-end)	Dark	8.5
6½ "	Light	0.0
16 " (overnight)	Dark	5.5

Although the fall of pressure in the light tended to zero, it was necessary to continue illumination at intervals in order that the fall of pressure in the dark should be maintained. There is here evidence that a photochemical equilibrium in the light is reached, involving an intermediate compound which subsequently decays in the dark.

At the end of the period allowed for the reaction, the nitrogen and the unchanged nitric oxide were measured, after all the other gases had been removed by absorption in soda. The "soda-equivalent" of the absorbed gases was determined by titration with standard acid, and expressed in c.c.  $N/10$  soda. The increase in "soda-equivalent" due to the absorbable product of the reaction could be obtained from a knowledge of the soda-equivalent of the initial quantity of cyanogen employed.

The quantity of nitric oxide used up, and the increase in soda-equivalent of the system, as a result of reactions I and II can be calculated from the measured fall of pressure and the quantity of nitrogen produced. Comparison of the calculated with the experimental figures establishes the accuracy of the equations. The calculation also gives the relative extents to which the two reactions occur, and is made in the following way:—

Let the quantities of the various substances involved in reactions I and II be expressed in terms of pressure, measured in mms. Hg, by  $a$  and  $b$  respectively as shown. It is then a simple matter to calculate  $a$  from the fall of pressure due to reaction I, making due allowance for the association of the nitrogen peroxide. If  $p$  is the total pressure of nitrogen peroxide and  $p_0$  the partial pressure of the monomeric form,  $\text{NO}_2$ , measured in mm. then the relation of Wourtzel<sup>4</sup> gives at 25° C.

$$\frac{p_0^2}{p - p_0} = 108 \quad \dots \quad \dots \quad \dots \quad \dots \quad (1)$$

The total nitrogen peroxide produced by reaction I, expressed wholly as monomeric  $\text{NO}_2$  is

$$2a = 2(p - p_0) + p_0 \quad \dots \quad \dots \quad \dots \quad \dots \quad (2)$$

Finally, if we represent the total observed fall in pressure by  $P$ , then

$$3a - p = P \quad \dots \quad \dots \quad \dots \quad \dots \quad (3)$$

These three equations enable us to calculate the unknowns  $a$  and  $p$ .

The value of  $b$  may then be obtained from the relationship

$$a + 3b = \text{observed pressure of nitrogen} \quad \dots \quad \dots \quad \dots \quad (4)$$

<sup>4</sup> Compt. Rend., 1919, 169, 1397.

From these values of  $a$  and  $b$  we may calculate:

- (1) the quantity of NO used up, as  $(4a + 4b)$ ,
- (2) the increase in soda-equivalent of the system, measured in c.c.  $N/10$  Soda, by the relationship  $\frac{2a + 4b - b}{760} \cdot \frac{273}{298} \cdot \frac{10000}{22400} \cdot \frac{130}{1} = 0.07(2a + 3b)$  ( $130$  c.c. being the volume of the reaction vessel and gauge),
- (3) the relative magnitudes of reactions I and II, measured in terms of NO used up, as  $a/b$ .

The results of these calculations for two runs are shown in Table II.

TABLE II.

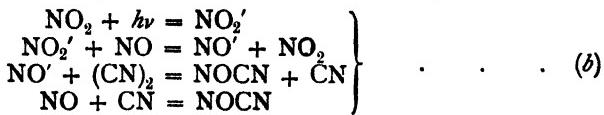
No.	Initial Pressure (mm.)		N <sub>2</sub> formed (mm.)	$a$ mm.s.	$b$ mm.s.	Gases Produced (mm.s. calc.)		NO used (mm.)		Increase in Soda Equiv. alent. (c.c. $N/10$ Soda).		
	NO.	(CN) <sub>2</sub>				NO <sub>2</sub>	CO <sub>2</sub>	Obs.	Calc.	Obs.	Calc.	
	NO.	(CN) <sub>2</sub>				NO <sub>2</sub>	CO <sub>2</sub>	Obs.	Calc.	Obs.	Calc.	
I	449	304.5	52	56	37.3	6.2	60	12.4	174	174	6.7	6.5
2	366	362	34.5	38	26.1	4.0	43.7	8.0	124	120.4	5.2	4.5

It will be seen from the values of  $a$  and  $b$  that reaction I is some six times as extensive as reaction II, while the agreement shown in the last four columns between observed and calculated values, satisfactorily establishes the validity of the equations employed.

### Mechanism of the Reaction.

The general equations established above do not indicate the mechanism by which the reaction between nitric oxide and cyanogen takes place. There are, however, a number of indications during the reaction of the existence of an intermediate compound. In the first place, under continued illumination, the fall of pressure ceases and the system apparently comes to a stationary state, which changes with further fall of pressure when the light is removed. In the second place, the Draper effect which develops is much greater than the maximum effect obtainable with nitrogen peroxide alone, e.g., 8 to 13 mm., whereas the maximum effect obtainable with nitrogen peroxide in the presence of excess nitric oxide in the same apparatus was but 7 mm.

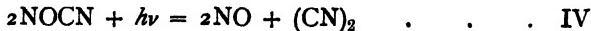
It has already been observed that a trace of oxygen is essential to the initiation of the reaction, and this in the presence of nitric oxide is equivalent to nitrogen peroxide. It is also notable that at the beginning, the reaction velocity as measured by the pressure fall in the light, increases as the nitrogen peroxide accumulates in the system. We therefore conclude that the reaction is dependent on nitrogen peroxide and is autocatalytic as this substance accumulates. There is, however, no direct reaction between cyanogen and nitrogen peroxide as was independently established by a separate experiment, and we are therefore forced to the conclusion that nitrogen peroxide plays the part either of a catalyst or photosensitiser. We shall assume that it makes possible the development of a comparatively unstable intermediate compound—the hitherto unknown nitrosyl cyanide—according to either of the following alternative schemes (a) and (b)—



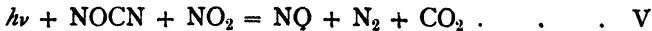
The net result of either scheme (a) or (b) is that nitrosyl cyanide is produced by the light, with a fall in pressure according to the equation



Nitrosyl cyanide itself, however, like nitrosyl chloride is to be regarded as unstable in the light and we should expect the reaction

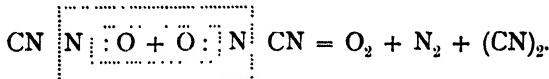


to occur with increase of pressure. The opposition of reactions III and IV would finally produce a photochemical stationary state, with which a Draper effect would be associated. This is in agreement with experimental finding, and accounts for the augmented Draper effect already mentioned. We shall also assume that nitrosyl cyanide is attacked in the light by nitrogen peroxide :—



This reaction is to be regarded in the nature of a side reaction to the main light changes and accounts for the production of carbon dioxide. Since it occurs with an increase of pressure, it also assists in the establishment of the photochemical stationary state. By combining reactions III and V we obtain finally reaction II.

The existence of a photochemical stationary state involves the development of an equilibrium quantity of the intermediate compound, nitrosyl cyanide during illumination. Experiment indicates, further, that a dark reaction coupled with a fall in pressure always follows the photochemical reaction when the light is removed, while nitrogen peroxide and nitrogen gradually accumulate in the system. We therefore postulate the breakdown of our intermediate compound in the dark, according to the scheme :—



The consequence of this is the gradual accumulation of nitrogen peroxide, by reaction of the oxygen produced with excess nitric oxide



so that the net dark reaction may be written



The fall in pressure is accounted for by the polymerisation of the nitrogen peroxide, and with the help of equation (1) can be used to calculate the quantity of nitrosyl cyanide present in the system on removing the light. Thus, in experiment (2) table (II.), in which the initial partial pressures of nitric oxide and cyanogen were each about  $\frac{1}{2}$  atmosphere, the system was illuminated for a period of  $6\frac{1}{2}$  hours, during which there was a pressure fall of  $13\frac{1}{2}$  mm. The light was then removed and there was a subsequent fall

of 21 mm. which extended over a period of nearly one week. It can easily be calculated by equation (1) that this fall of pressure in the dark corresponds to the production of 90 mm. of  $\text{NO}_2$  in the monomeric form, and therefore to the presence of 90 mm. of nitrosyl cyanide at the end of the period of illumination.

Attempts were made to separate nitrosyl cyanide from the system by the use of different freezing mixtures. It was not found possible to condense it at  $-20^{\circ}\text{ C}.$  by a freezing mixture of concentrated hydrochloric acid and ice, but it was frozen out at  $-78^{\circ}\text{ C}.$  by solid carbon dioxide and ether. In the presence of such easily condensable substances as cyanogen, nitrogen peroxide and dinitrogen trioxide, however, no separation could be effected by this means.

There remain two further facts for explanation—

(1) From table (I.) it will be seen that as the reaction proceeds, the fall of pressure in succeeding dark periods becomes less and less. This is accounted for if we remember that as nitrogen peroxide is gradually accumulating in the system, reaction V comes more into prominence, and the equilibrium quantity of nitrosyl cyanide must become correspondingly smaller.

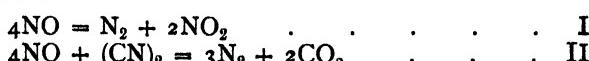
(2) The increase in Draper effect often observed in the system after standing overnight in the dark is similarly explained by the accumulation of nitrogen peroxide, which, since it acts as a photosensitiser to the main light reaction III automatically increases its velocity and therefore the heat effect associated with the equilibrium of the opposed reactions III and IV. This small increase in the Draper effect dies away again as the photochemical equilibrium is re-established in the system and excess nitrogen peroxide is removed by reaction V.

Although the net reactions I and II are in themselves slow, it is probable that both reactions III and IV become rapid as nitrogen peroxide becomes established in the system. This in fact must be the case since, undoubtedly, large quantities of the intermediate compound accumulate when the photostationary state is reached. There is therefore every probability that a large Draper effect will be associated with the equilibrium.

The mechanism suggested above is believed to explain all the observed facts. The phenomena associated with this change are so varied and apparently disconnected that the success of the simple mechanism proposed make it something more than speculative, and it is claimed renders probable the postulated existence of nitrosyl cyanide as an intermediate compound.

### **Summary.**

When a mixture of nitric oxide and cyanogen, each at  $\frac{1}{2} - \frac{1}{3}$  atm. partial pressure, is illuminated by ultra-violet light of  $360 - 220\mu\mu$  the following reactions occur:—



The former reaction is about six times as extensive as the latter.

In reaction I, cyanogen plays the part of a catalyst, but neither reaction occurs in the absence of a small trace of oxygen, *i.e.* nitrogen peroxide. This latter gradually accumulates as the reaction proceeds, the effect being autocatalytic.

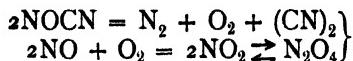
A dark reaction occurring over several days with fall of pressure continues after the light has been cut off, and indicates the existence of a

comparatively stable intermediate compound which is believed to be nitrosyl cyanide NOCN. This is probably produced with fall of pressure in the system according to the two opposed photo-reactions

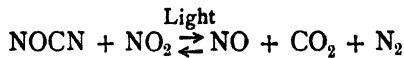


the forward reaction being catalysed or sensitised by  $\text{NO}_2$ . These reactions give rise to a photochemical stationary state associated with considerable equilibrium pressures (*e.g.* 90 mm.) of  $\text{NO}\text{CN}$ .

Nitrosyl cyanide itself, being unstable, decays spontaneously in the dark according to the scheme :



which in combination with reaction III gives the total change represented by reaction I. Reaction II results as a side reaction by combining the change,



with reaction III.

The mechanism proposed for this change is illustrative of the working of a catalyst (cyanogen) in a homogeneous reaction promoted by a trace of oxygen, and occurring with the formation of an unstable intermediate compound (nitrosyl cyanide).

A precisely similar series of changes which can be explained by an analogous mechanism has been observed in the system nitric oxide—cyanogen chloride. An account of this will be given at a later date.

Our thanks are due to the Chemical Society for the loan of the quartz vessel and microscope used in this work.

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## PART III. NEUTRAL SALT AND ACTIVITY EFFECTS.

### THE THEORY OF ACID AND BASIC CATALYSIS.

By J. N. BRÖNSTED.

*Received 23rd July, 1928.*

In the Arrhenius theory of electrolytic dissociation the catalytic effect of acids and bases was interpreted as a direct kinetic influence of the hydrogen and hydroxyl ions. Later and more intensified studies on catalytic phenomena have given rise to modifications and extensions in the original point of view, the most important of which are briefly presented in the first section of the present article. The modern ideas about "salt effect" are discussed in section 2, and in section 3 an extended theory of acid and basic catalysis is enounced.

Part of the material in this paper has been more elaborately treated in some of the chapters of a monograph on the subject to which the reader is referred for details.<sup>1</sup>

#### 1. Previous Theories.

Lapworth<sup>2</sup> seems to be the first to recognise that the hydrogen ion in water solution exists as a hydrate. He conceived an equilibrium between the hydrate and the free ion and ascribed the catalytic effect exclusively to the latter. On this basis he was able to account satisfactorily for the phenomenon, found by Goldschmidt,<sup>3</sup> that small quantities of water exert a pronounced anti-catalytic effect on reactions catalysed by hydrogen ions in alcoholic solution.

The same ideas were strongly advocated by Rice.<sup>4</sup> However, since it is now known that the free ("dry") hydrogen ion is identical with the hydrogen nucleus and, as may be judged by its enormous heat of hydration, has no possibility of existing in solution, it obviously can exert only a negligible kinetic effect. Realising the correctness of this conclusion Rice<sup>5</sup> has recently suggested the existence of another "modification" of the free hydrogen ion possessing a heat of hydration much smaller than that of the ordinary ion. There seems to be no evidence, either theoretical or experimental, in favour of this idea.

Goldschmidt<sup>6</sup> himself explained the anti-catalytic effect of water by regarding the alcoholate of the hydrogen ion as the catalytic active agent,

<sup>1</sup> Brönsted, *Om Syre- og Basekatalyse*, Københavns Universitets Festschrift, 1926. A translation of this article appears in the *Chemical Reviews* 5, 231, 1928.

<sup>2</sup> Fitzgerald and Lapworth, *J. Chem. Soc.*, 93, 2163 (1908); Lapworth, *ibid.*, 93, 2187 (1908).

<sup>3</sup> Goldschmidt, *Ber.*, 28, 3218 (1895); 29, 2208 (1896).

<sup>4</sup> Rice, *J. Amer. Chem. Soc.*, 45, 2808 (1923).

<sup>5</sup> Rice, "The Mechanism of Homogeneous Organic Reactions," 1928, p. 75.

<sup>6</sup> Goldschmidt, *Z. Elektrochemie*, 15, 4 (1909).

this on addition of water being converted into a less active hydrate. We shall find corroboration for this view in section 3. It constitutes, in fact, a first step towards a more general theory of acid and basic catalysis.

An idea which has played a considerable part in the discussion of catalysis is the so-called "dual theory of catalysis," advanced by a great number of authors.<sup>7</sup> This theory originates in the fact that addition of neutral salts to a solution, where a reaction proceeds under the influence of acids or bases, usually causes a pronounced acceleration of the reaction to take place. The classical example is that found by Arrhenius; the inversion of cane sugar in the presence of a weak acid, say acetic acid. If 0.1M sodium chloride is added to such a solution the velocity increases about 30 per cent. If sodium acetate be added instead of NaCl the dissociation of the acid is thrown back; the decrease in velocity, however, is much less than calculated by the mass action law; in other words, in this case also there is an accelerating salt effect. Such phenomena would be explicable, at least qualitatively, if one attributed to the "undissociated" acids a catalytic effect parallel to that of the hydrogen ion.

In developing this "dual theory of catalysis," however, two factors have been overlooked. The first of these is the *medium effect*. The velocity constant of a reaction is not the same in pure water and in a tenth molar salt solution. Secondly, it is a consequence of the modern theory of solutions that the mass action law in its classical form cannot be applied in correctly calculating ionic concentrations. When using the classical mass action law, results which foreshadow an effect due to undissociated acids are just what one would anticipate. It can therefore be asserted that the dual theory has been established on the basis of a misinterpretation of the underlying experimental facts. This subject will be dealt with more thoroughly in the discussion of the various salt effects in the second section of this article.

A third theory, which may be called the ionisation theory of acid and basic catalysis, has been proposed particularly by Euler<sup>8</sup> and Stieglitz.<sup>9</sup> According to this theory the mechanism of the effect of the hydrogen and hydroxyl ions can be described as an instantaneous reaction ("salt formation") of the ions with the substrate (catalyst), the measurable reaction being the subsequent "spontaneous" change of the ion thus formed.

For instance when hydroxyl ions are added to a solution of  $\alpha$ -glucose, owing to the acid character of this substance, glucose anions are formed. The rapid mutarotation reaction shown by the solution is explained by Euler, by assigning to the glucose anion thus formed a high degree of reactivity. This conforms to the view commonly held (but certainly not justified), that ionic reactions are more rapid than reactions between electrically neutral molecules.

It will be realised, first, that the mechanism suggested cannot be distinguished from the mechanism of an ordinary bimolecular reaction between the molecules of the catalyst and the substrate. The impossibility of such a distinction appears quite conclusively by application of the mass action laws of equilibrium and velocity, not only in their classical form, but also when the modern modifications of these laws are applied. The conformity

<sup>7</sup> Acree, *Amer. Chem. J.*, **37**, 410 (1907); **38**, 258 (1907). Snethlage, *Z. physik. Chem.*, **85**, 252 (1913). Dawson, *J. Chem. Soc.*, **103**, 2135 (1913); **107**, 1426 (1915). Taylor, *Z. Elektrochem.*, **20**, 291 (1914), etc.

<sup>8</sup> Euler, *Z. physik. Chem.*, **32**, 348 (1900); **36**, 641 (1901). Numerous recent papers in *Z. anorg. Chem. and Z. physik. Chem.*

<sup>9</sup> Stieglitz, *J. Amer. Chem. Soc.*, **32**, 221 (1910); **35**, 1774 (1913).

of the ionisation theory with the experimental facts cannot therefore be taken as evidence in favour of its validity.

This argument of course also applies to the special case in which the substrate undergoing chemical change is ionised to a *large* extent by the hydrogen and hydroxyl ions added. Skrabal,<sup>10</sup> who has criticised the ionization theory, as well as Euler<sup>11</sup> himself, seems to be of opinion that reactions of this kind are particularly fitted for testing the ideas of this theory. No device applied to *special* cases is, however, able to invalidate the above general conclusion.

On the other hand, so long as those reactions are considered in which only hydrogen and hydroxyl ions are active catalysts the ionisation theory of catalysis cannot be dismissed as a possible interpretation of the catalytic mechanism in special cases. Nor can the criticism advanced by Lowry<sup>12</sup> be taken as in all respects cogent. The most serious objections to it as a general theory are provided by the extended catalytic theory which is presented in section 3.

By many authors, particularly Harned<sup>13</sup> and his co-workers, an attempt has been made to apply the *activity* concept in connection with catalytic phenomena. Åkerlöf,<sup>14</sup> in a study of reactions catalysed by hydroxyl ions has brought out the parallelism between the catalytic effects and the activity of the catalysts in concentrated salt solution. Kuhn and Jacob,<sup>15</sup> in conscious opposition to the theory presented in section 2, take the activity of the hydrogen ion to be the determining factor in the glucose mutarotation reaction. Also Taylor and Close<sup>16</sup> from results obtained in an investigation on lactose formation in ether and water seem inclined to measure the catalytic effect by the hydrogen ion activity. The inadequacy of such assumptions has, however, been thoroughly demonstrated from both experimental and theoretical points of view.<sup>17</sup> In connection with the last mentioned investigation, in which is considered the velocity in two liquid layers in equilibrium, it should be realised that ionic activities in such layers are not necessarily equal.

## 2. The Kinetic Salt Effect.

The great majority of catalytic reactions occur in solutions of ions. As the presence of ions even in great dilution materially alters the properties of a solution any serious study of catalytic phenomena requires full recognition of the *kinetic salt effect*.

First, it should be recalled that addition of salts alters the medium, and simply for that reason affects the velocity constant. The changes in the nature of the medium caused by salts are particularly marked, but we have every reason to believe that this effect is linear with salt concentration in the dilute range. More insight into the nature of the effect of salts upon catalytic reactions is obtained by means of the general theory of reaction

<sup>10</sup> Skrabal, *Z. Elektrochem.*, **33**, 322 (1927).

<sup>11</sup> Euler und Ölander, *Z. physik. Chem.*, **131**, 107 (1927); cf. also Ölander, *ibid.*, **129**, 3 (1927).

<sup>12</sup> Lowry, *J. Chem. Soc.*, 1927, 2554.

<sup>13</sup> Harned, *J. Amer. Chem. Soc.*, **40**, 1461 (1918); **44**, 1475 (1922); **44**, 2193 (1922).

<sup>14</sup> Åkerlöf, *J. Amer. Chem. Soc.*, **48**, 3046 (1926).

<sup>15</sup> Kuhn und Jacob, *Z. physik. Chem.*, **113**, 389 (1924).

<sup>16</sup> Taylor and Close, *J. physical Chem.*, **24**, 1085 (1925).

<sup>17</sup> Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); **115**, 337 (1925).

velocity in solution.<sup>17</sup> According to this theory the velocity of a bimolecular reaction between the molecules A and B is given by the expression :

$$v = k c_A c_B \frac{f_A f_B}{f_X} . . . . . \quad (1)$$

$f_A$  and  $f_B$  denoting the activity coefficients of A and B, and  $f_X$  the activity coefficient of a critical complex X, formed by collision of these molecules. This formula has proved to be in accordance with facts in a great number of ionic reactions in which the *kinetic activity factor*  $\frac{f_A f_B}{f_X}$  is particularly sensitive towards changes in salt concentration. In such cases we speak about an *exponential salt effect*, the kinetic activity factor, according to formula (2), varying in proportion to the square root of the salt concentration. In the case of a hydrogen ion catalysis A may mean the non-charged molecule of the substrate, B the hydrogen ion and X consequently a complex possessing one positive charge. Expressing the activity coefficient of a molecule by means of the formula<sup>18</sup>

$$-\log f = 0.5z^2 \sqrt{\mu} + \beta \mu . . . . . \quad (2)$$

where  $\mu$  is the ionic strength, we obtain for the above case of hydronium catalysis :

$$v = k c_A c_B e^{\mu(\beta_A + \beta_H - \beta_X)} . . . . . \quad (3)$$

This corresponds to a *linear* salt effect in the dilute range. As the  $\beta$ -factor for the hydrogen ion is unusually large (and therefore probably larger than  $\beta_X$ ) and for a non-charged molecule usually positive, we have reason to expect a positive salt effect in a hydrogen ion catalysis, as actually found for such reactions.

A linear salt effect in conformity with the requirements of formula (3) exists in the classical examples of the cane sugar inversion and ester

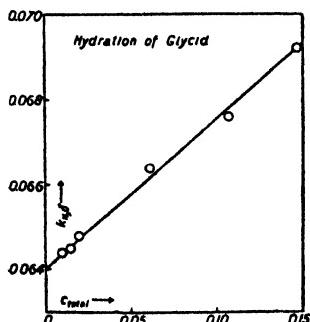


FIG. 1.

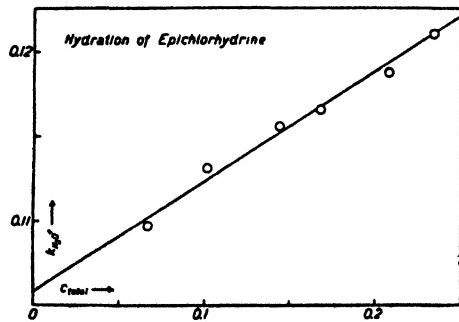


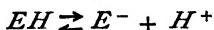
FIG. 2.

hydrolysis. It has also been found in a number of recent investigations, for instance in the decomposition of diazoacetic ester, nitrosotriacetoneamine, etc. Here should be given some new data found by Mary Kilpatrick who studied in this laboratory the hydration of ethylene oxide and similar compounds under the catalytic influence of perchloric acid. The results are given as plots, from which the linearity of the salt effect appears clearly. The effect in these reactions is unusually large.

<sup>18</sup> Cf. Brönsted, *Trans. Farad. Soc.*, **23**, 416 (1927).

It has been mentioned that some authors suppose hydrogen ion catalysis to be determined not by the concentration but by the activity of this ion. This theory not only disagrees with formula (1) but is in marked disconformity with the linear salt effect found in the experiments just mentioned. It is evident from equation (2) that the activity of the hydrogen ion as the determining factor in catalysis would mean the existence of an exponential salt effect for instance in the hydrolysis of cane sugar by acids and in similar reactions. In this connection it is also significant to observe that the electrometric  $p_H$  scale frequently used for presenting kinetic experiments is unfitted for this purpose, as it is actually an activity, not a concentration scale.

The salt effect dealt with so far is a direct kinetic effect which has been termed *primary kinetic salt effect*. Salt addition, however, may also give rise to a change in reaction velocity by changing the concentrations of the reacting molecules, and in such cases we speak about *secondary kinetic salt effect*.<sup>19</sup> For instance, in a solution of a weak acid like acetic acid or in an acetic acid-acetate buffer the hydrogen ion concentration changes upon addition of salts. When to the equilibrium in question



the thermodynamic mass action law is applied:

$$\frac{c_E - c_{H^+}}{c_{EH}} \cdot \frac{f_E - f_{H^+}}{f_{EH}} = K \quad . \quad . \quad . \quad . \quad . \quad (4)$$

the magnitude of the effect is easily computed in the dilute range by means of equation (2).

To the previous numerous verifications of the theory of secondary salt effect should be added here some experiments by W. F. K. Wynne-Jones in

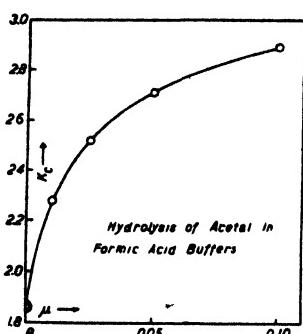


FIG. 3.

this laboratory on the hydration of acetal, a reaction which has been previously studied by Skrabal<sup>20</sup> from a different point of view. This reaction is a pure hydrogen ion catalysis and shows, when a strong acid is used as catalyst, a primary salt effect of normal sign and magnitude. When a weak acid is used as a catalyst a marked secondary salt effect is exhibited, corresponding very closely to the change in the dissociation constant computable from equation (3). The results are shown in the accompanying graph (Fig. 3).

The secondary kinetic salt effect obviously depends not only upon the electric

value (compare sect. 3), strength and concentration of the acid, but also upon the ratio in which the buffer constituents are present. It manifests itself, therefore, in a very diversified manner, and it is necessary to give full consideration to it in order to avoid misinterpretation of kinetic phenomena.

It has already been mentioned that the dual theory of catalysis originated

<sup>19</sup> Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924); Brönsted and Teeter, *J. physical Chem.*, **28**, 579 (1924); Brönsted and King, *J. Amer. Chem. Soc.*, **47**, 2523 (1925).

<sup>20</sup> Skrabal and Mirtl, *Z. physik. Chem.*, **III**, 98 (1924).

in such a misinterpretation of effects caused by addition of salts to a buffer system, or simply by changing the concentration of an ion, which forms a constituent of the buffer. Even in recent work on catalysis the theory here in question is often entirely neglected; for instance, Dawson<sup>21</sup> maintains the point of view that salt effect can legitimately be neglected, and on this basis attempt to calculate for instance the effect of undissociated acids in ester hydrolysis. Quite recently, however, Dawson<sup>22</sup> seems to have come to a fair recognition of both primary and secondary salt effect and provides a valuable experimental contribution to the problem.

### 3. An Extended Theory of Acid and Basic Catalysis.

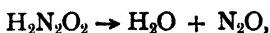
The extended theory of acid and basic catalysis rests upon a new definition of acids and bases and upon the contention that the hydrogen ion or proton does not exist in a free state in solution. The new definition of acids and bases<sup>23</sup> referred to is represented by—



the molecules A and B (which may bear any charge compatible with this scheme) being termed *conjugate* acids and bases. From this definition it is evident, first, that the basic properties cannot be reserved for the hydroxyl ion alone, as has been the general opinion heretofore. Furthermore, if the hydrogen ion exists in water as the hydrate  $\text{H}_3\text{O}^+$ , and similarly in other solvents in a solvated state, acid properties can to no greater extent be monopolised by any special molecule. Both the "hydrogen" and hydroxyl ion are molecules to which, according to the above scheme, acid or basic properties can be assigned; they possess, however, no unique position as acids and bases. The conspicuous part admittedly played by these ions in the doctrine of acids and bases is based upon practical rather than theoretical qualifications.

The consequences of these ideas for acid and basic catalysis are obvious. If we are justified in ranging the hydrogen and hydroxyl ions amongst ordinary acids and bases we cannot preserve for them a unique position as catalysts. The effect exerted by "hydrogen" and hydroxyl ions must be a general effect possessed by all acid and basic molecules. From the picture of the acid basic function, given by scheme (5), the mechanism of catalysis is then at once visualised as being essentially a transfer of a proton from catalyst to substrate (acid catalysis) or from substrate to catalyst (basic catalysis). We should expect, therefore, the catalytic activity in a given reaction to depend upon the readiness with which this transfer takes place, and this again is connected with the strength of the catalyst as an acid or a base.

The first reaction in which general acid or basic catalysis is unquestionably demonstrated is the *nitramide* decomposition studied by Brönsted and Pedersen.<sup>19</sup> It was found that nitramide decomposes slowly in aqueous solution according to



but this reaction is markedly accelerated by the presence of basic molecules. For instance 1/100 molal acetate ion solution in mixture with 1/100 molal acetic acid (to keep the hydroxyl ion concentration low) increases the

<sup>21</sup> Dawson and Lawson, *J. Chem. Soc.*, 1927, 2444.

<sup>22</sup> Dawson and Key, *J. Chem. Soc.*, 1928, 1239, 1248.

<sup>23</sup> Brönsted, *Rec. Pays Bas.*, 4, 718 (1923); *J. physical Chem.*, 30, 777 (1926).

velocity more than tenfold. Similar catalytic effect was shown by a great number of other negatively charged bases, aniline and other amines and hydroxo-ions belonging to the group of cobalt ammines and carrying two positive charges. In a subsequent paper,<sup>24</sup> the phenomena observed in nitramide catalysis were recognised as being of a general nature, and from this point of view, on the basis of the new definition of the conception of acids and bases, the general theory of acid and basic catalysis was developed in detail.<sup>1</sup>

Further evidence in support of the theory was brought by Dawson and Carter,<sup>25</sup> who studied the reaction between acetone and iodine in buffer solutions. As these authors do not consider salt effects adequately and do not distinguish between activity and concentration, their numerical calculations are open to criticism.<sup>26</sup> However, the effect of the constituents of the buffer in this reaction are so marked that there is no doubt as to the character of their results.

Another reaction which has proved of great value for the new theory of catalysis is the mutarotation reaction of *glucose*. The influence of a great number of acids and bases of various electric types on the velocity of this reaction has been studied by Brönsted and Guggenheim<sup>27</sup> who showed the kinetics of the reaction to conform entirely to the ideas of the extended theory. Lowry and Smith<sup>28</sup> studied the same reaction, particularly from the point of view of the theory of "prototropic change." Such a change is effected by the presence of acids and bases simultaneously. If, therefore, an acid acts as a catalyst in the mutarotation the reaction takes place by the simultaneous influence of the solvent as a base and *vice versa*. Catalysis in which the simultaneous presence of acids and bases is required we shall term *amphoteric catalysis*. Where a comparison is possible the numerical results of Lowry and Smith agree with those of Brönsted and Guggenheim, but the value given for HCl cannot be accepted since it rests on the classical dissociation data of the acid.

The acetone-iodine reaction also may be classed amongst the prototropic changes. There is no reason to believe, however, that the extended theory should preferably be limited to such reactions as Lowry<sup>29</sup> seems to think. The nitramide decomposition, for instance, which is very sensitive towards bases, is apparently not catalysed by acids. The converse is true for the hydrolysis of *ethyl orthoacetate*, which is catalysed by acids and not by bases. This reaction which is extremely sensitive to hydrogen ions has been studied recently in this laboratory by Wynne-Jones, who found a marked effect of the weak acids from which the buffers, used for the experiments, were prepared.

Thus a considerable amount of evidence is already accumulated in support of the view that acid and base molecules in general show catalytic properties similar to those which have been attributed to the hydrogen and hydroxyl ions. It may be possible on that basis to account for kinetic phenomena not as yet understood. Thus in the work of Taylor and Close quoted above<sup>16</sup> the effect of water in an ether solution of hydrochloric acid may be explained as amphoteric catalysis, HCl (or an ether compound thereof) acting as an acid and H<sub>2</sub>O as a base. Addition of water to the dry HCl solution will therefore accelerate the reaction strongly. On the

<sup>24</sup> Brönsted and Duus, *Z. physik. Chem.*, **117**, 299 (1925).

<sup>25</sup> Dawson and Carter, *J. Chem. Soc.*, 1926, 2282.

<sup>26</sup> The same criticism applies to many other recent investigations, see for instance Duboux et Frommet, *J. Chim. Physique*, **24**, 245 (1927).

<sup>27</sup> Brönsted and Guggenheim, *J. Amer. Chem. Soc.*, **49**, 2554 (1927).

<sup>28</sup> Lowry and Smith, *J. Chem. Soc.*, 1927, 2539.

<sup>29</sup> Lowry, *J. Chem. Soc.*, 1927, 2554.

other hand, by increasing amounts of water the acid  $\text{H}_3\text{O}^+$  will be converted in the weaker acid  $\text{HCl}$  which causes the velocity to decrease. In cases of that sort there is of course also the possibility of a large medium effect. It would be of very considerable interest to extend the experiments to those non-aqueous solutions (for instance, benzene solutions) in which, owing to its non-basic character, "hydrogen ions" cannot be present. There can hardly be any doubt that the interesting observations of strongly catalytic influences which have occasionally been made in such solvents, for instance as regards various mutarotation reactions,<sup>30</sup> may be interpretable from the point of view of this theory.

A question of greatest importance for the extended theory here set forth is the dependence of catalytic efficiency upon the strength of the catalyst as an acid or a base. In view of the mechanism suggested above one would expect the catalytic constant to increase with the strength. When we remember that the dissociation constant of an acid must be given as the ratio of two velocity constants, which determine the speed of dissociation and association,

$$\frac{k_{\text{diss}}}{k_{\text{ass}}} = K_A$$

it becomes probable that the catalytic constant  $k_A$  for acid catalysis is related to the kinetic constant of dissociation more directly than to  $K_A$ . On the further assumption that in a series of isotropic acids the two constants  $k_{\text{diss}}$  and  $k_{\text{ass}}$  co-operate in producing the changes in  $K_A$ , i.e. that increase in  $k_{\text{diss}}$  is accompanied by decrease in  $k_{\text{ass}}$ , passing from one member to another, the relation :

$$k_A = G_1 K_A^x \quad . \quad (6)$$

where  $k_A$  is the catalytic constant and  $K_A$  the dissociation constant of an acid,  $G$ , a constant for the

<sup>30</sup> Lowry, *J. Chem. Soc.*, **93**, 107 (1908); Lowry and Richards, *ibid.*, **127**, 1385 (1925).

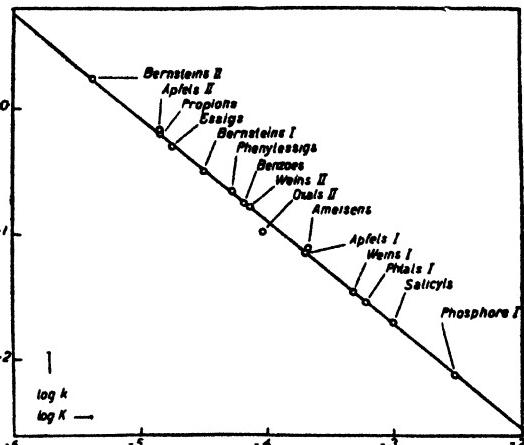


FIG. 4.

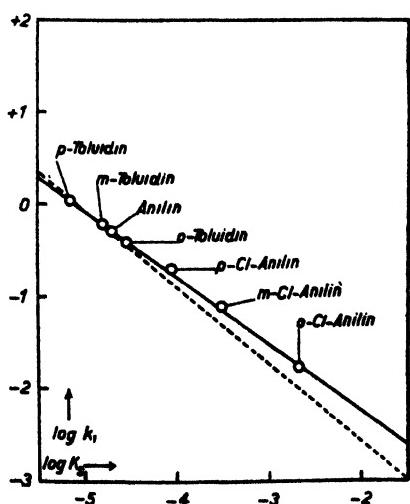


FIG. 5.

reaction considered and  $1 > \gamma > 0$ , seems plausible from a theoretical point of view. In the case of basic catalysis the corresponding expression is

$$k_B = G_2 K_B^\gamma \quad \dots \quad \dots \quad \dots \quad \dots \quad (7)$$

$\gamma$  again representing a proper fraction.

This relation has proved of a remarkable applicability in the decomposition of nitramide. The plot of  $\log k_A$  against  $\log K_A$  in this case comes out as a straight line with a slope of  $0.8$ , which is the value of  $\gamma$  in the above equation, the value of  $G_2$  being  $6.2 \times 10^{-5}$ . It makes little difference in these values if electrically neutral bases or bases with one or two negative charges are considered, as shown by the diagram Figs. 4 and 5. The dotted line in Fig. 5 is identical with the full line in Fig. 4. In the case of bases with two positive charges (for instance  $[CoOH(NH_3)_5]^{++}$ ), the ex-

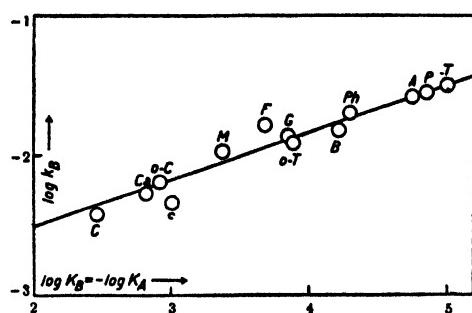


FIG. 6.—Dependence of basic catalysis on the strength of the basic anion (glucose).

T, trimethylacetate Ph, phenylacetate; G, glycolate; S, salicylate; C, cyanacetate; P, propionate; B, benzoate; F, formate; o-C, o-chloro-benzoate; A, acetate; o-T, o-toluate; M, mandelate; Ca, chloroacetate.

ponent  $\gamma$  and therefore the slope of the straight line is again the same, but the absolute catalytic activity ( $G_2$ ) is much higher.

Also for the mutarotation the above equations seem to hold at least approximately. The slope of the straight line in the logarithmic plot is here about  $0.4$  for the basic and about  $0.2$  for the acid catalysis (Figs. 6 and 7). Here the influence of the electric type, to be expected theoretically, and also statistical effects,<sup>10, 1</sup> have been omitted. There is further evidence of the applicability of the equation in other reactions studied in the laboratory (see Fig. 8), and we are perhaps justified in expecting that for acids and bases of the same type it may be fairly exact. Even if it should prove to be only an approximation when applied as a general formula, this would be of great kinetic significance.

Here attention should be called to a point of particular importance. In a number of cases a reaction, catalysed by hydrogen or hydroxyl ions, also proceeds with a measurable speed in pure water solution. Such

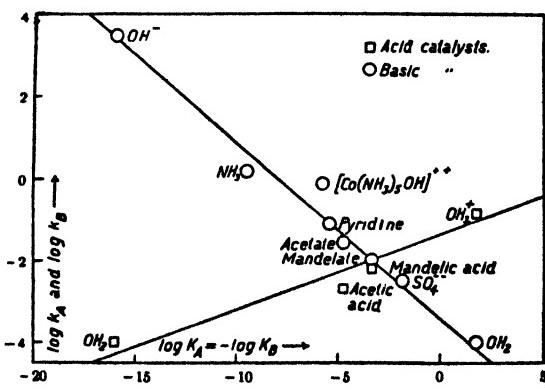


FIG. 7.—Dependence of acid and basic catalysis on the strength of acid and base (glucose).

"spontaneous reactions" may very well be classed as cases of acid or basic catalysis, the properties of the solvent molecules being both acid and basic. Thus the slow spontaneous decomposition of nitramide in acid solution may be considered the result of basic catalysis by the water molecules. In fact when calculating the velocity constant from this point of view we find it actually to fit formula (7) satisfactorily. Very striking is also the agreement in the case of the mutarotation of glucose (Fig. 7) and the hydrolysis of ethyl orthoacetate (Fig. 8), all the points, including the value of water catalysis, being approximately located on a straight line. In the first of these reactions the straight line relation holds good through a range of  $10^{18}$  in  $K_A$ . That the water point is on the lines for both acid and basic catalysis is good evidence that the mutarotation at any composition of the solution is effected by what we have called amphoteric catalysis.

If one accepts this view of the "spontaneous" reaction it is obviously possible from the water reaction and hydrogen catalysis to calculate with approximation the general acid catalysis constant for any acid of known strength. Applying equation (6) to three acids and eliminating  $G_1$  and  $x$  from the three equations thus obtained we get the general equation

$$\log \frac{k_1}{k_2} = \log \frac{k_3}{k_2} \cdot \frac{\log \frac{K_1}{K_2}}{\log \frac{K_3}{K_2}} \quad \dots \quad \dots \quad \dots \quad (8)$$

which for acid (1) = A, acid (2) =  $H_2O$ , and acid (3) =  $H_3O^+$  gives  $K_2 = 1.5 \times 10^{-16}$ ,  $K_3 = 55$ , and therefore :

$$\log \frac{k_A}{k_{H_3O^+}} = 0.06 \log \frac{K_A}{55} \log \frac{k_{H_3O^+}}{k_{H_2O}} \quad \dots \quad \dots \quad \dots \quad (9)$$

or  $\log \frac{k_A}{k_{H_2O}} = 0.06 \log \frac{K_A}{1.5 \cdot 10^{-16}} \log \frac{k_{H_3O^+}}{k_{H_2O}} \quad \dots \quad \dots \quad (10)$

Having measured  $k_{H_3O^+}$  and  $k_{H_2O}$ , the molal velocity constants for hydrogen ion catalysis and water reaction, it is thus possible to determine the catalysis constant  $k_A$  of any acid of known strength ( $K_A$ ). The condition necessary for the practical detection of acid catalysis is of course that it is not of a much lower order of magnitude compared to the hydrogen ion and water catalysis. Estimation of relative velocities of acid catalysis and hydrogen ion or water catalysis in a buffer solution A,B can be made on the basis of the relations :

$$\begin{aligned} \frac{v_A}{v_{H_3O^+}} &= \frac{k_A}{k_{H_3O^+}} \cdot \frac{c_A}{c_{H_3O^+}} \\ \log \frac{v_A}{v_{H_3O^+}} &= 0.06 \log \frac{K_A}{55} \log \frac{k_{H_3O^+}}{k_{H_2O}} + \log \frac{c_B}{c_A} \quad \dots \quad \dots \quad (11) \end{aligned}$$

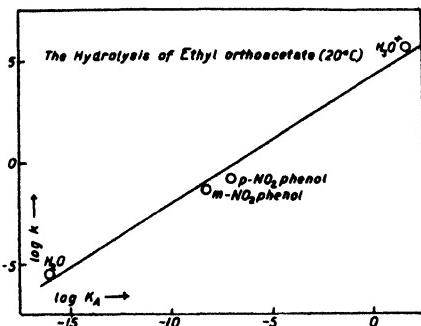


FIG. 8.

and

$$\frac{v_A}{v_{H_2O}} = \frac{k_A}{k_{H_2O}} \frac{c_A}{c_{H_2O}}$$

$$\log \frac{v_A}{v_{H_2O}} = 0.06 \log \frac{K_A}{1.5 \cdot 10^{-16}} \log \frac{k_{H_2O^+}}{k_{H_2O}} + \log \frac{c_A}{55} \quad . \quad (12)$$

where  $c_A$  and  $c_B$  are the concentrations of conjugate acid and base in the buffer. Analogous equations can of course be derived for basic catalysis.

Putting  $K_A = 100$  and  $c_B = 1$ :

$$\log \frac{v_A}{v_{H_2O^+}} = 0.02 \log \frac{k_{H_2O^+}}{k_{H_2O}} - 2.$$

From  $1 > x > 0$  follows  $17.5 > \log \frac{k_{H_2O^+}}{k_{H_2O}} > 0$ . The maximum value of

$\log \frac{v_A}{v_{H_2O^+}}$  is therefore  $-1.7$ . With still stronger acids the ratio  $\frac{v_A}{v_{H_2O^+}}$

becomes smaller. The catalysis in water solution, by very strong acid, for instance HCl, will therefore hardly be perceptible compared to that of the hydrogen ion, the decrease in  $c_A$  more than compensating the increase in  $k_A$ .

Decreasing strength of acid increases the value of  $\frac{v_A}{v_{H_2O^+}}$  and from this point of view, therefore, increases the probability of detecting acid catalysis. On the other hand, by decreasing strength of acid the water reaction as shown by formula (12) is more likely to interfere.

There may exist cases in which the water reaction can not, or can only in part, be classed as a catalytic reaction in the sense here spoken of. In such cases we cannot expect formulæ (11) and (12), to hold. For all reactions studied in this laboratory, however, the appearance of a water effect is connected with the presence of acid or basic catalysis in conformity with the extended theory.

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## CATALYTIC EFFECTS OF ACIDS AND BASES AND THE INFLUENCE OF INERT SALTS.

BY HARRY MEDFORTH DAWSON.

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The idea that the hydrogen and hydroxyl ions are differentiated from other positive and negative ions in their capacity to act as catalysts is consistent with much of the early work on the influence of acids, bases, and salts on the velocity of chemical change. Such observations seemed to show that the catalytic effect is simply proportional to the concentration of the hydrogen ion in acid solutions and to the concentration of the hydroxyl ion in alkaline solutions. Since the product of the concentrations of these

ions is constant for dilute aqueous solutions it was to be expected that both ions would be catalytically effective under certain conditions of acidity, and from a study of the auto-catalysis of methyl acetate in its early stages,<sup>1</sup> it was possible to show that the reaction velocity passes through a minimum value which is attained when the concentration of the hydrogen ion is such that the partial velocities due to the hydrogen and hydroxyl ions are equal.

For other reactions, e.g. the hydrolysis of sulphonic esters<sup>2</sup> it was found that the reaction velocity is not appreciably affected by changes in the hydrogen ion concentration, and to explain the observed constant speed in acid solutions, it seemed necessary to admit that the velocity of the uncatalysed reaction is very appreciable or that undissociated water molecules act as catalysts in the reaction.

Certain well-known anomalies, e.g. the increase in the catalytic power of the strong acids on the addition of the corresponding salts made it further necessary to assume the existence of specific "salt effects," for the explanation of which various hypotheses were brought forward.

More recent investigations of catalytic effects produced by acids have shown clearly, however, that the facts cannot be interpreted in terms of the catalytic action of hydrogen ions, hydroxyl ions, water molecules and the "salt effects" referred to.

For example, the velocity of the acetone-iodine reaction with 0.5*N* acetic acid as catalyst is about twice as great as the velocity which would be expected on the basis of the hydrogen ion concentration, and in this solution the catalytic effects attributable to the hydroxyl ion and the water molecule are negligibly small. Discrepancies of this kind, which resulted in part from observations on the variation of the catalytic activity of free acids with the concentration, and in part from observations on the changes produced by the addition of the corresponding salts, led to the conclusion that the unionised acid is partly responsible for the observed catalytic effect.<sup>3</sup>

On the writer's suggestion this modified view became known as the dual theory, and the evidence advanced in its support was such as to warrant the belief that the dual theory of acid catalysis represented a definite advance on the classical hydron theory.

Unpublished observations on the acetone-iodine reaction with mixtures of acetic acid and sodium acetate had already shown in 1915 that the dual theory was inadequate to explain the data obtained with such mixtures, although the results obtained in parallel experiments with mixtures of chloracetic acid and sodium chloracetate showed no marked deviations from the requirements of this theory.<sup>4</sup> When increasing quantities of sodium acetate are added to a solution of acetic acid of fixed concentration, it was, indeed, found that the reaction velocity does not approach asymptotically to a limiting minimum value as required by the dual theory in the absence of disturbing "salt effects," but passes through a fairly sharp minimum, beyond which the velocity increases linearly with the salt concentration. The facts were subsequently confirmed and their interpretation led to the view that catalytic effects must be ascribed to the acetic ion as well as to the acetic

<sup>1</sup> Wijs, *Z. physikal. Chem.*, 1893, II, 492; 12, 514.

<sup>2</sup> Wegscheider and Furcht, *Monatshefte*, 1902, 23, 1093; Praetorius, *ibid.*, 1905, 26, 1.

<sup>3</sup> Goldschmidt, *Z. physikal. Chem.*, 1910, 70, 687; *Z. Elektrochem.*, 1911, 17, 684; Bredig, Millar, and Braune, *Z. Elektrochem.*, 1912, 18, 535; Snetlage, *ibid.*, 1912, 18, 539; Dawson and Powis, *J. Chem. Soc.*, 1913, 2135; Taylor, *Medd. K. Vetensk. Nobel-inst.*, 2, Nr. 34, 35, 37.

<sup>4</sup> Cf. Dawson and Reiman, *J. Chem. Soc.*, 1915, 1426.

acid molecule.<sup>5</sup> For a mixture of acid and salt represented by  $c\text{HA} + x\text{MA}$ , where  $c$  is constant and  $x$  variable, the reaction velocity may therefore be represented by the equation

$$v = k_h^+ [\text{H}] + k_a^- [\text{A}] + k_m [\text{HA}] \quad . . . . \quad (1)$$

and if HA is a weak acid and  $x$  not too small, by

$$v = k_h^+ [\text{H}] + k_a x + k_m c \quad . . . . \quad (1a)$$

where  $[\text{H}] = Kc/x$ . For the linear portion of the  $v$ - $x$  curve, the first term in equation (1a) may be neglected, and by differentiation we obtain

$$dv/dx = k_a$$

and by extrapolation of the line to  $x = 0$ ,

$$v = k_m c.$$

In other words, the slope of the linear portion of the curve gives the catalytic coefficient  $k_a$ , whilst the intercept on the zero ordinate gives  $k_m$ , if the catalytic effect of undissociated water can be neglected. Since the value of  $k_h$  can be derived from experiments with hydrochloric acid at low concentrations, it is apparent that these observations yield values for all the coefficients which find expression in equation (1). For the acetone-iodine reaction at  $25^\circ$  and an acetone concentration of 20 c.c. per litre, the values are  $k_h = 4.65 \times 10^{-4}$ ,  $k_a = 4 \times 10^{-6}$  and  $k_m = 1.5 \times 10^{-6}$ . The corresponding coefficient for undissociated water<sup>6</sup> is  $k_w = 1.3 \times 10^{-10}$ .

#### Evaluation of $k_a$ and $k_m$ from Experiments with Isohydric Solutions.

The relations considered above are those which are shown by series of mixtures for which the concentration of the acid is constant. The evaluation of  $k_a$  and  $k_m$  may also be effected by making use of the data for mixtures characterised by constancy of the ratio  $c/x = q$ . For a given value of  $q$  the reaction velocity for the corresponding series of mixtures may be written

$$v = v_0 + k_a x + k_m c = v_0 + (k_a + qk_m)x \quad . . . \quad (2)$$

where  $v_0$  is the velocity in the absence of acid and salt, at a hydrogen ion concentration, which for a given acid HA is determined by the value of  $q$ . According to this equation,  $v$  is a linear function of  $x$ . If  $l$  denotes the slope of the  $v$ - $x$  line and  $l'$  the slope for mixtures characterised by the ratio  $c/x = q'$  we have

$$k_a + qk_m = l \quad \text{and} \quad k_a + q'k_m = l'$$

whence

$$k_a = \frac{l'q - lq'}{q - q'} \quad \text{and} \quad k_m = \frac{l - l'}{q - q'}$$

Actual experiments with acetic acid-acetate mixtures have shown that the reaction velocity for such isohydric mixtures is a linear function of the salt (or acid) concentration and the values derived for  $k_a$  and  $k_m$  from the data are in close agreement with those already recorded.

With regard to  $v_0$  it may be pointed out that this, in the general case, corresponds with the sum of the catalytic effects which are due to the

<sup>5</sup> Cf. Dawson & Carter, *J. Chem. Soc.*, 1926, 2282.

<sup>6</sup> Cf. Dawson & Key, *J. Chem. Soc.*, 1928, 543.

hydrogen ion, hydroxyl ion, and water molecule as expressed by the equation

$$v_0' = k_h[\overset{+}{\text{H}}] + k_{\text{OH}}[\overset{-}{\text{OH}}] + k_w[\text{H}_2\text{O}]$$

Since  $k_h[\overset{+}{\text{H}}] = k_{\text{OH}}[\overset{-}{\text{OH}}]$  when  $v_0'$  is a minimum, it follows that systematic measurements of this kind will permit of the determination of  $k_w$  and  $k_{\text{OH}}$ .

### Catalytic Activity of the Free Acid in its Dependence on the Concentration.

The value of the coefficient  $k_m$  may also be derived from experiments on the catalytic activity of the acid at different concentrations. For such solutions  $[\overset{+}{\text{H}}] = [\overset{+}{\text{A}}]$ , and equation (1) may be put in the form

$$v = (k_h + k_a - k_m)[\overset{+}{\text{H}}] + k_m c \quad . . . . \quad (3)$$

If the strength of the acid is such that the hydrogen ion concentration is given with sufficient accuracy by  $[\overset{+}{\text{H}}] = \sqrt{Kc}$ , this equation may be written

$$v/\sqrt{c} = (k_h + k_a - k_m)\sqrt{K} + k_m \sqrt{c} \quad . . . . \quad (4)$$

according to which  $v/\sqrt{c}$  is a linear function of  $\sqrt{c}$ . The slope of this line thus gives  $k_m$ , whilst the intercept on the zero ordinate gives  $(k_h + k_a - k_m)\sqrt{K}$ . If  $k_a$  is known, or if it can be neglected in comparison with  $k_h$ , it is obvious that the ionisation constant  $K$  of the acid may be derived from the intercept. When the strength of the acid is such that the substitution of  $\sqrt{Kc}$  for  $[\overset{+}{\text{H}}]$  is not permissible, equation (3) may be put in the form.

$$v/\sqrt{c}(1 - a) = (k_h + k_a)\sqrt{K} + k_m \sqrt{c(1 - a)} \quad . . . . \quad (5)$$

where  $a$  is the degree of ionisation of the acid.

In this case, a preliminary value of  $K$  may be obtained by the use of equation (4), and this may be used to derive the values of  $\sqrt{c(1 - a)}$  necessary for the plot of  $v/\sqrt{c(1 - a)}$  against  $\sqrt{c(1 - a)}$ . The slope of the line corresponding with equation (5) gives  $k_m$  and the intercept  $(k_h + k_a)\sqrt{K}$ . If necessary, the procedure described may be repeated.

Experiments of this kind have given values of  $k_m$  which accord well with those derived from the observations made with acid-salt mixtures of the constant acid type and of the isohydric type. The values of  $K$  are, moreover, in close agreement with the ionisation constants derived from conductivity measurements.

To illustrate the nature of the results obtained by the application of equations (4) and (5) reference may be made to the data for glycollic acid. In this case the plot of  $v/\sqrt{c}$  against  $\sqrt{c}$  gives  $k_m = 6.0 \times 10^{-6}$  and  $(k_h + k_a - k_m)\sqrt{K} = 5.4 \times 10^{-6}$ , whence the preliminary value of  $K$  is  $1.38 \times 10^{-4}$ .

The graph corresponding with equation (5) then gives  $k_m = 5.7 \times 10^{-6}$  and  $(k_h + k_a)\sqrt{K} = 5.70 \times 10^{-6}$ , whence  $K = 1.50 \times 10^{-4}$ , which is identical with the value given by conductivity data.<sup>7</sup>

In reference to the methods described above for the determination of

<sup>7</sup> Ostwald, *Z. physikal. Chem.*, 1889, 3, 170.

catalytic coefficients, it is to be noted that the results generally are consistent with one another. In particular the values obtained for  $k_m$  are the same whether the solutions concerned contain the corresponding salt or are salt free.

### Co-ordination of the Catalytic Data for Acid-salt Mixtures of the Constant Acid Type.

In the further consideration of the data for acid-salt mixtures of the type  $c\text{HA} + x\text{MA}$  ( $c$  constant and  $x$  variable), it may be pointed out that in virtue of the relations

$$[\bar{A}] = K(c - [\bar{H}]) / [\bar{H}] \text{ and } [\text{HA}] = c - [\bar{H}]$$

equation (1) may be put in the form

$$v = (k_h - k_m)[\bar{H}] + k_aKc / [\bar{H}] + k_m c - k_aK . . . . . (5)$$

according to which, since  $c$  is constant, the reaction velocity for the series depends only on the hydrogen ion concentration. The term  $k_aK$  would appear to represent a negligibly small quantity. By differentiation, it may be shown that the velocity passes through a minimum when the hydrogen ion concentration has the value given by

$$[\bar{H}]_i = \sqrt{k_aKc / (k_h - k_m)} . . . . . (6)$$

By substitution in equation (5), the minimum reaction velocity  $v_i$  is found to be expressed by

$$v_i = 2\sqrt{(k_h - k_m) \cdot k_aKc} + k_m c . . . . . (7)$$

$$= 2(k_h - k_m) \cdot [\bar{H}]_i + k_m c . . . . . (7a)$$

The particular acid-salt mixture for which these relations obtain has been termed the M.V. or iso-catalytic mixture. This is further characterised by the equality of the partial velocities which are due respectively to the hydrogen ion and the acid anion.

From equation (5) we obtain

$$dv/d \log [\bar{H}] = (k_h - k_m) \cdot [\bar{H}] - k_aKc / [\bar{H}] . . . . . (8)$$

from which it follows that the curve obtained by plotting  $v$  against  $\log [\bar{H}]$  should be symmetrical with reference to the iso-catalytic point. The curve in question is a catenary, and from the symmetry it follows that the logarithm of the hydrogen ion concentration of the iso-catalytic solution is the arithmetic mean of the logarithms of the hydrogen ion concentrations  $[\bar{H}]_1$  and  $[\bar{H}]_2$  of any pair of solutions belonging to the same constant acid series for which the reaction velocities are equal.

In other words,  $[\bar{H}]_1 \cdot [\bar{H}]_2 = [\bar{H}]_i^2 . . . . . (9)$

The experimental data for acetic acid-acetate mixtures have been shown to conform to these symmetry requirements for both the acetone-iodine reaction<sup>8</sup> and the hydrolysis of ethyl acetate.<sup>9</sup>

For each value of  $c$  in the constant acid series of mixtures represented by  $c\text{HA} + x\text{MA}$  there is a corresponding catenary for which the iso-catalytic

<sup>8</sup> Dawson and Dean, *J. Chem. Soc.*, 1926, 2872.

<sup>9</sup> Dawson and Lawson, *ibid.*, 1927, 2444.

data are given by equations (6) and (7). The investigation of the acetone-iodine reaction in reference to acetic acid-acetate mixtures with values of  $c$  ranging from 0.01 to 1.0 mols per litre, has shown that the iso-catalytic data vary with the acid concentration in close correspondence with the requirements of these equations.<sup>10</sup> Deviations which are clearly in excess of those that could be attributed to experimental error, were only met with in the case of the most concentrated acid solution. Substantial evidence has thus been obtained for the applicability of equation (5) as an expression of the relation between the reaction velocity and the hydrogen ion concentration for acid-salt mixtures of the constant acid type.

Since all mixtures of the acid HA and the corresponding salts can be grouped into such series, it follows that the entire catalytic relations can be represented by a series of juxtaposed catenaries, the combination of which gives rise to a catenary surface in space defined by co-ordinates which correspond respectively with reaction velocity, hydrogen ion concentration and concentration of the catalysing acid.<sup>11</sup>

### The Generalised Catalytic Catenary.

For any constant acid series of acid-salt mixtures in which the acid is relatively weak, the variations in the velocity expressed by equation (5) are due to changes in the catalytic effects produced by the positive and negative ions. Denoting the ionic reaction velocity by  $u$ , where  $u = v - k_m c$ , we have

$$u = (k_h - k_m) \cdot [H] + k_a Kc / [H] . . . . . \quad (10)$$

and if the hydrogen ion concentration  $[H]$  for any solution of the series is expressed in terms of the hydrogen ion concentration  $[H]_i$  of the corresponding iso-catalytic solution, such that  $n = [H]/[H]_i$ , then equation (10) may be written

$$u = (k_h - k_m)n[H]_i + k_a Kc/n[H]_i,$$

and since  $[H]_i = \sqrt{k_a Kc/(k_h - k_m)}$   
we obtain  $u = \sqrt{(k_h - k_m)k_a Kc} \cdot (n + 1/n) . . . . . \quad (11)$

If, further, the ionic reaction velocity is expressed in terms of the corresponding velocity for the iso-catalytic mixture, such that  $r = u/u_i$ , then since  $u_i = 2\sqrt{(k_h - k_m)k_a Kc}$

we obtain  $r = \frac{1}{2}(n + 1/n) = \cosh \log n . . . . . \quad (12)$

which expresses quite generally the connection between the reduced ionic reaction velocity  $r$  and the reduced hydrogen ion concentration  $n$ .<sup>12</sup>

Equation (12) contains no specific constants and the relation between  $r$  and  $\log n$  corresponds with a catenary curve. The general equation thus affords an expression of the relation between reaction velocity and hydrogen ion concentration, which is apparently independent of the nature and concentration of the catalysing acid, of the temperature, of the solvent medium and of the nature of the acid catalysed reaction. Even when the conditions are such that the anionic catalysis is shared by

<sup>10</sup> Dawson and Hoskins, *J. Chem. Soc.*, 1926, 3166.

<sup>11</sup> Compare Dawson, *J. Chem. Soc.*, 1927, 756.

<sup>12</sup> Cf. Dawson, *J. Chem. Soc.*, 1927, 213.

the anions of the dissolved acid and those of the solvent the relation is still valid.<sup>13</sup>

The tests which have been made of the applicability of the generalised catalytic formula cover a wide range of variations and the degree of concordance with experiment is such as to justify the view that the reduced catenary affords a satisfactory account of the relations which are associated with the joint action of any combination of catalytically active entities which conform to the specified stoichiometric conditions.<sup>12</sup>

### Effects Produced by Catalytically Inert Salts.

In the methods which have been followed in the above-described interpretation of the experimental observations and in the derivation of the equations which would seem to afford a satisfactory basis for the co-ordination of catalytic effects, no account has been taken of what may be conveniently referred to as inert salt effects. In particular, it has been assumed that the ionisation constant of the catalysing acid is not thereby affected. This assumption was necessarily tentative, but for a preliminary survey of the field it was extremely convenient. It was always realised, however, that developments of the research might render it necessary to modify this simple assumption.

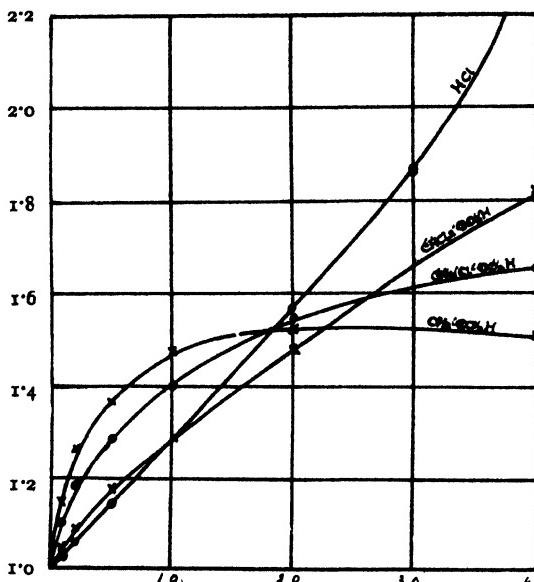


FIG. 1.—Influence of inert salt on catalytic activity of acids in 0.1 N solution. Velocity expressed in each case in terms of the velocity for the salt free solution. Abscissa give concentration of sodium chloride in moles per litre.

In this connection, attention may now be directed to experiments which have been made on the effects produced by the addition of catalytically inert salts to solutions of various acids. Arrhenius<sup>14</sup> showed that the catalytic activity of a weak acid is increased under such circumstances and suggested that this was due to increased ionisation, a view which has been supported by Brönsted.<sup>15</sup> More recent work has included a comparative examination of salt effects for acids ranging in strength from hydrochloric to acetic in which the concentration of the added salt (sodium chloride) has been raised to 4.0 mols per litre.<sup>16</sup> From the curves which are obtained by plotting

<sup>13</sup> Cf. Dawson, *J. Chem. Soc.*, 1927, 1146.

<sup>14</sup> *Z. physikal. Chem.*, 1899, 31, 197.

<sup>15</sup> *J. Chem. Soc.*, 1921, 574.

<sup>16</sup> Dawson and Key, *J. Chem. Soc.*, 1928, 1239.

the reaction velocities for  $0.1\text{N}$  solutions of the catalysing acid against the salt concentration, it is apparent that there is a gradual change in the character of the inert salt effect as the strength of the catalysing acid changes. For hydrochloric acid, the relations are represented by a straight line up to nearly  $3.0$  mols salt per litre; at higher salt concentrations the velocity increases more rapidly. For the three weaker acids examined—dichloracetic, chloracetic and acetic—there is a very marked departure from linearity which increases as the strength of the acid diminishes. At low salt concentrations, the inert salt effect is greatest for acetic and least for hydrochloric, but the order of the acids is reversed when the salt effects at the highest concentration are compared. The differences in the behaviour of the various acids are seen by inspection of Fig. 1, in which the observed velocities for each acid are expressed in terms of the corresponding velocity for the salt-free solution.

On the assumption that the data for hydrochloric acid afford a measure of the catalytic activity of the hydrogen ion in presence of the catalytically inert salt, it is possible to calculate the concentration of the hydrogen ion and from this the ionisation constants of the partially ionised acids in the salt solutions. If  $k_a$  denotes the catalytic coefficient for the hydrogen ion in a solution which contains  $c$  mols HA and  $x$  mols inert salt per litre, then equation 3 may be written

$$v = (k_x + k_a - k_m)[H] + k_m c$$

$$\text{whence } [H] = (v - k_m c) / (k_x + k_a - k_m) \quad . \quad . \quad . \quad (13)$$

from which the ionisation constant of the acid in the various salt solutions is obtained by substitution of this value of  $[H]$  in  $K = [H]^2 / (c - [H])$ .

The values of  $k_a$  and  $k_m$  which are required in the application of equation (13) may be derived for the salt solutions by the methods already described. The results obtained for acetic acid ( $0.1\text{N}$ ) in sodium chloride and sodium nitrate solutions are shown in Table I.

TABLE I.

## SODIUM CHLORIDE.

$x$ .	$v \cdot 10^6$ .	$k_x \cdot 10^4$ .	$[H] \cdot 10^6$ .	$K \cdot 10^6$ .
—	0.777	4.65	1.35	1.82
0.2	0.975	4.91	1.68	2.82
0.5	1.055	5.30	1.71	2.91
1.0	1.143	5.95	1.67	2.79
2.0	1.180	7.26	1.42	2.02
4.0	1.165	11.10	0.91	0.84

## SODIUM NITRATE.

	$0.777$	$4.65$	$1.35$	$1.82$
0.1	0.923	4.74	1.63	2.66
0.5	1.025	5.11	1.71	2.93
1.0	1.060	5.57	1.635	2.67
2.0	1.070	6.48	1.42	2.02
4.0	1.030	8.30	1.035	1.07

It is clear from the above figures that the ionisation constant of the acid increases at first with the addition of salt, but diminishes in the more concentrated solutions. The maximum value of  $K$  represents approximately a 50 per cent. increase and is reached when the salt solution is roughly of 0.5 molar concentration. Similar results have been obtained for chloracetic acid.<sup>17</sup>

The relations are obviously closely similar to those afforded by the potential difference measurements of Harned<sup>18</sup> who was led to the conclusion that the ionisation constant of water passes through a maximum when gradually increasing quantities of the alkali chlorides are added. The relative effects produced by potassium, sodium, and lithium chlorides show indeed a close correspondence in the two cases.

Catalytic and potential measurements would thus seem to agree in showing that the ionisation constant of an acid is appreciably affected by its ionic environment. The dependence of  $K$  on the salt concentration would seem to indicate that two different factors are involved, and it has been suggested<sup>16</sup> that the increase of the ionisation constant at low salt concentrations is due to the localised interactions between the molecules of the weak electrolyte and the ions of the salt. These molecules are of the polar type and on the average the positive poles will be in closer proximity to the negative ions than to the positive ions. In the same way, the negative poles will be nearer on the average to the positive ions. The polar molecules will thus be subjected to forces which increase the tendency to ionisation. The effect in question may be expected to increase at first with the number of the ions which are present in unit volume, but it seems probable that the influence of the individual ion effect will ultimately be over-shadowed by that due to the entire group of positive and negative ions which are within range of the polarisable molecule and in the limit it would appear that the dielectric capacity of the surrounding medium and possibly other environmental factors will be mainly responsible for the degree of ionisation of the weak electrolyte.

The investigation of the catalytic activity of partially ionised acids in salt solutions has thus shown that there are two distinct effects involved in the action of catalytically inert salts. The first is represented by an increase in the catalytic activity of the hydrogen ion and the second by a change in the ionisation constant of the acid. The former increases continuously with the salt concentration, whilst the ionisation constant increases to a maximum value and then decreases.

The question now arises as to how far these effects influence the interpretation of the results for acid-salt mixtures which have been co-ordinated and explained on the assumption that inert salt effects can be left out of account. The answer to this question so far as weak acids are concerned has been furnished by the investigation of the catalytic activity of free acetic acid, and also of acetic acid-acetate mixtures in solutions containing 0.1, 0.5, 2.0 and 4.0 mols sodium chloride per litre.<sup>19</sup> The relations shown by the free acid at different concentrations, by isohydric mixtures of acid and salt, and also by constant acid series of mixtures are sensibly the same for these

<sup>17</sup> Results obtained by Harned and Hawkins, *J. Amer. Chem. Soc.*, 1928, 50, 85, in the study of the hydrolysis of esters with mono- and di-chloracetic acids as catalysts show that the ionic activity coefficients product ( $\gamma$ ) passes through a minimum with increasing salt concentration. Since  $K$  is inversely proportional to  $\gamma$  it follows that the observations are quite analogous.

<sup>18</sup> *Z. physikal. Chem.*, 1924, 28, 579.

<sup>19</sup> Dawson and Key, *J. Chem. Soc.*, 1928, 1248.

salt solutions as when pure water is used as solvent. The velocity can be equally well represented by the equation

$$v = k_h [\overset{+}{H}] + k_a [\overset{-}{A}] + k_{OH} [\overset{-}{OH}] + k_m [\overset{-}{HA}] + k_w [\overset{-}{H_2O}]$$

in which the hydroxyl and water terms need not be considered. When  $k_a$  and  $k_m$  are evaluated by the methods previously described it is found that these coefficients are but slightly affected by the presence of the inert salt. This constancy of  $k_a$  and  $k_m$  is in marked contrast to the large variations which are associated with  $k_h$ . The reason for this difference in susceptibility to ionic environment is by no means apparent. It may possibly be connected with the complex nature and relative instability of the "hydrogen" ion as represented by variations in its proton donating capacity.

In the following table the values of  $k_h$ ,  $k_a$ ,  $k_m$  for the various solvents used are compared. The  $k_m$  values were derived by the application of equation (4) and the  $k_a$  values by the method described in connection with equation (1a).

TABLE II.

Solvent.	$k_h \cdot 10^4$ .	$k_a \cdot 10^4$ .	$k_m \cdot 10^4$ .	$\log [\overset{+}{H}]_i$ .	$v_i \cdot 10^4$ .
Water	4.65	4.0	1.4	4.05	0.267
0.1 NaCl	4.78	4.0	1.4	4.12	0.278
0.5 "	5.30	3.7	1.4	4.17	0.288
2.0 "	7.26	3.4	1.4	4.01	0.280
4.0 "	11.10	3.4	1.3	5.65	0.237

When the observed reaction velocities for mixtures of the type  $\alpha\text{CH}_3\text{CO}_2\text{H} + \beta\text{CH}_3\text{CO}_2\text{Na}$  are plotted against the logarithm of the hydrogen ion concentration, the latter being calculated in the usual way from the appropriate  $K$  value, catenary curves are obtained for all the solvents. The displacements produced by the inert salt are relatively small, as may be seen from the values of  $\log [\overset{+}{H}]_i$  and  $v_i$  for the several iso-catalytic mixtures which are recorded in the fifth and sixth columns of the preceding table. The degree of symmetry of the catenaries, as tested by equation (9), is in all cases very close and the shift of the iso-catalytic point with the concentration of the inert salt bears an obvious relation to the corresponding change in the ionisation constant of the acid.

When the reaction velocities are calculated from equation (1) it is found that the agreement between these and the observed velocities is even better for the sodium chloride solutions than for pure aqueous solutions of the acetic acid-acetate mixtures. This is probably connected with the circumstance that the inert salt effect of the acetate will be more in evidence when pure water is the solvent than in the case when the solvent already contains a considerable quantity of salt in the form of sodium chloride.

The general conclusion to be drawn from the experiments with solutions of catalytically inert salts is that the latter do not markedly affect the nature of the relations which find expression in the symmetrical catenary curves as applied to weak acids. The catalytic effects described and co-ordinated by the author cannot therefore be regarded as effects which are to be explained away by the replacement of the molar concentration of the hydrogen ion by its thermodynamic equivalent.

The only further point which will be discussed relates to the question of the circumstances under which primary catalytic effects may be interfered

with, or even obscured by inert salt effects. In the first place, much depends on the nature of the catalysed reaction. The relative values of  $k_h$ ,  $k_a$ , and  $k_m$  for a given acid vary very widely from one reaction to another. In aqueous solution, the magnitudes of  $k_{OH}$  and  $k_w$  must also be considered, and even if the intervention of the hydroxyl ion is ruled out by the degree of acidity of the solution, it is apparent that the investigation of the effects which are associated with  $k_a$  and  $k_m$  is facilitated when the values of these coefficients are not too small in relation to  $k_h$  and  $k_w$ .

For the acetone-iodine reaction the relative values of the various coefficients are such as to permit of the study of the individual catalytic effects, and this is also true of the mutarotation of glucose which has been successfully examined by Lowry and Smith<sup>20</sup> and by Brönsted and Guggenheim,<sup>21</sup> who have shown that complex positive ions of the same type as the "hydrogen ion" may also act as catalysts.

Assuming that a suitable reaction has been found for the detailed study of the effects associated with the undissociated molecule HA and the anion A, we may proceed to the consideration of the influence of inert salts, dealing in the first instance with constant acid mixtures of the type  $\epsilon$ HA +  $x$ MA. In this connection it should be kept in mind that  $k_a$  and  $k_m$  are but slightly affected by the presence of inert salts. Whether this is generally true has of course to be proved by further experiments.

If now HA is a weak acid, the concentration of the hydrogen ion will be greatly reduced by the addition of small quantities of the corresponding salt, and favourable conditions are thereby provided for the manifestation of the

effects which are due to HA and A. In view of the small concentration of the hydrogen ion for such a series of solutions when  $x$  is very small the changes in the values of  $k_h$  and  $K$ , which result from the presence of the ions, will have comparatively little influence on the observed catalytic effects. Under these circumstances, there is no real difficulty in understanding the close agreement between the experimental results obtained with acetic acid-acetate mixtures and those derived theoretically on the assumption that inert salt effects can be neglected. The relations summarised in the catalytic catenary would thus appear to be but slightly affected by changes in the ionic strength of the solution in so far as the acid concerned is a weak acid.

If, on the other hand, the acid HA is a comparatively strong acid, the hydrogen ion concentration of the corresponding acid-salt mixtures will in general be so large that the observed catalytic effects are bound to be affected to a greater or less extent by those changes in  $k_h$  and  $K$  which depend on the ionic strength of the solution. Since  $k_a$  diminishes and  $k_m$  increases with the ionisation constant of the acid, it is possible that the inert salt effects may entirely prevent the determination of  $k_a$ , although the evaluation of  $k_m$  may be a relatively simple matter.

If, again, HA represents one of the strongest acids (e.g. HCl) it would seem that the change produced by the addition of the corresponding salt is almost entirely confined to that particular inert salt effect which finds expression in the stimulation of the catalytic activity of the hydrogen ion.

Turning now to the consideration of the influence of ionic environment on the variation of the catalytic activity of an acid with its concentration in salt free solutions, it may be noted that the inert salt effect in this case is due-

<sup>20</sup> *J. Chem. Soc.*, 1927, 2539.

<sup>21</sup> *J. Amer. Chem. Soc.*, 1927, 49, 2554.

to ions which are produced by the ionisation of the acid itself, and in regard to this influence there is some evidence to show that the changes associated with the ionic environment provided by the ionised acid may be comparatively small in comparison with the average effect produced by salt solutions of the same ionic strength. Furthermore it should be noted that in the case of the more concentrated solutions of weak and moderately strong acids, the increase of  $K$ , which results from the increased ionic concentration, is counteracted by the influence of the non-ionised molecules of the acid which tend to reduce the degree of ionisation of the acid. In the experiments with the acetone-iodine reaction, the solutions always contained a small quantity of potassium iodide and this would tend to stabilise the value of  $K$  in so far as the influence of ionic environment is concerned.

The above considerations serve in some measure to define the conditions under which it is permissible to interpret the results of catalytic experiments according to the procedure which has been followed by the author in previous work on the subject. The intervention of inert salt effects implies certain limitations in the extension of this procedure to the stronger acids, but the suggestion that the catalytic effects, which have been fully described in previous papers, may be explained in terms of variations of the thermodynamic concentration (activity) of the hydrogen ion, is obviously quite inadmissible. The experimental evidence which bears directly on the question of the catalytic activity of the hydrogen ion seems indeed to show that this is directly proportional to its volume concentration.<sup>22</sup>

<sup>22</sup> Dawson and Lawson, *J. Chem. Soc.*, 1928, 2146.

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## COMPOUNDS BETWEEN CATALYSTS AND SUBSTRATES AND THEIR REACTIVITY.

By H. v. EULER.

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The present paper will be confined to one group of homogeneous reactions, namely the hydrolysis by acids and bases in dilute aqueous solution. One can hardly deny that acid and basic substances play the largest and practically the most important rôle as hydrolysing catalysts.

The essential points in our actual knowledge upon the kinetics of catalysed hydrolyses were discovered during the first era of the theory of electrolytic dissociation. Wilhelm Ostwald's discovery of the parallelism between the conductivity of acids or bases and their catalytic action was soon followed by the statement, that this action is proportional to the concentration of the  $H^+$  and  $OH^-$  ions respectively. Within the limits in which this proportionality holds—we shall see that these limits are quite confined—the reaction velocity  $v$  may be expressed at all times by the formulæ

$v = \text{substrate} \times h$ , and  $v = \text{substrate} \times oh$  respectively, if  $h$  and  $oh$  designate the concentrations of the ions  $H^+$  and  $OH^-$ .

After this important progress the development of our knowledge of general homologous catalysis entered into a period of stagnation. No means had been discovered to connect the reaction velocity of a hydrolysable body with its other physical or chemical constants, and it was not even possible to predict qualitatively which substrate could be split by acids or bases or by both.

The theoretical treatment of catalysis was therefore merely formal. In most descriptions of chemical kinetics we find expressed the view that the catalysing  $H^+$  and  $OH^-$  ions act as a contact substance. The theories and hypotheses which have been put forward to explain the nature of catalysis are numerous; this is not the place to make a comparison between them.

I conceive that the main object is to find out the quantitative connections between measurable individual constants of catalyst and substrate on the one hand and the reaction velocity on the other. The chief problem of chemical kinetics, in my view, is solved when it is possible to calculate in advance the reaction velocity of a catalytic system from the concentrations and from the individual constants of catalyst and substrate.

With my co-workers—I may only refer to the research work of Erik Rudberg and of Arne Ölander—I have collected experimental facts on different kinds of hydrolytic reactions, and thereby made use of the hypothesis, that *acids and bases, when catalysing hydrolytic reactions, form compounds of the type of salts with their substrates, the catalyst being added to just that group of the substrate in which the hydrolysis takes place.* We assume that the electric charge gives to these groups of atoms a tendency to split and, consequently, we assume that *in this charged or ionic state the substrate is much more reactive than otherwise.*<sup>1</sup>

I wish to emphasise at once the following point: In those cases in which the dissociation constants  $K_a$  or  $K_b$  of the substrate are larger than  $10^{-15}$  it is possible experimentally to measure the degree of salt formation by the catalyst. Therefore in these cases we know the concentration of substrate ions and we can experimentally find the proportionality between this kind of molecule and the reaction velocity. Therefore I consider it logical to regard these ions as the interacting kind of molecules and as the cause of the (catalytically) increased reaction velocity.

### Glucose and Carboxyl-Esters as Amphoteric Electrolytes.

Knowing from many researches and especially from the interesting results of Lowry<sup>2</sup> that mutarotation behaves in a manner very similar to hydrolysis, I choose the mutarotation of glucose (instead of hydrolysis proper) as an example of my general idea.

As is known, glucose is a weak acid with the dissociation constant (at  $20^\circ$ )  $K_a = 65 \times 10^{-13}$ . According to this constant glucose combines with alkali to give glucosates and forms glucosate-ions to a degree easily calculated from the principles of the dissociation theory. Consequently we can calculate the concentration of glucosate-ions at different  $p_H$  and, doing so, we come to the experimental statement, that the velocity of mutarotation increases (between  $p_H = 8.5$  and  $p_H = 11.5$ ) proportionally to the concentration of glucosate-ions. We know the concentration of the glucosate-

<sup>1</sup> This was expressed in 1899 as follows: "Catalysis consists in the increase of one or several of those kinds of molecules by which the reaction proceeds through the formation of intermediate compounds, or in the increase of the interacting substrate-ions." (*Svenska Vet. Akad. Forhandl.*, 4.)

<sup>2</sup> *J. Chem. Soc.*, 1903, 83, 1316; 1925, 127, 1371; *II. Cons. Chim. Solvay*, 1925.

anions in the solution and therefore we can calculate their specific reactivity  $r\eta$ . This is expressed by the first terms of the formula—

$$k_1 + k_2 = k_0 + r\eta_1 \cdot K_a/h + r\eta_2 \cdot \frac{K_b}{K_w} \cdot h.$$

I wish to emphasise that our values  $r\eta$  are determined in aqueous solutions and that evidently other values will be found in other solvents.

The conclusion that between  $p_H = 8.5$  and  $p_H = 11.5$  the increasing concentration of glucosate-ions is the cause of the increasing reaction velocity seems to me to be not only logical but most natural, and thus we calculate a value for the specific reactivity of the glucosate-ions,  $r\eta = 66$  (at  $20^\circ$ ), which corresponds to a half life period of  $0.27$  sec.

As we find from the formula for the mutarotation of glucose, the reactivity of the glucosate-ion is very much larger than the reactivity of the free glucose. However, the reactivity of the free glucose has a definite value, which is expressed by the term  $k_0 = 0.0012$ .

From our fundamental hypothesis of 1899<sup>3</sup> I drew the conclusion, in 1920,<sup>4</sup> that the substrates, hydrolysable as well by acids as by bases, must be amphoteric electrolytes, being able to combine with both kinds of catalyst. The total reactivity of the substrate therefore is represented by the products of concentration and specific reactivity of at least three kinds of molecules, namely of

- (1) the free substrate molecules.
- (2) the substrate-anions.
- (3) the substrate-cations.

Besides these three kinds of molecules others may be formed in the presence of neutral salts, and they may take part in the total reaction in proportion to their specific reactivity.<sup>5</sup>

Attention is drawn to the above result, that the reactivity of the glucosate-ion is very large compared with the reactivity of the free substrate. Making the preliminary and simplifying assumption that the specific reactivity of glucose-anions  $r\eta_1$  is equal to that of glucose-cations  $r\eta_2$ , we come to the (probably inexact) conclusion that the minimum of mutation velocity, found between  $p_H = 2$  and  $p_H = 8$  represents the minimum of glucose ions, and we find the minimum of reaction velocity at the iso-electric point to be

$$h = \sqrt{\frac{K_a}{K_b} K_w}$$

In all cases, where  $r\eta_1$  is not equal to  $r\eta_2$  we have to introduce these values as correcting factors to  $K_a$  and  $K_b$ .

The exact expression of the reaction velocity is according to the hypothesis of interacting ions

<sup>3</sup> Euler, *Öfvers. Sv. Vet. Akad. Förh.*, 1899, 4; *Z. physik. Chem.*, 32, 348, 1900; 36 641, 1901.

<sup>4</sup> Euler and Laurin, *Sv. Vet. Akad. Ark. f. Kemi*, 7, 30.

<sup>5</sup> In such cases, where the reactivity is increased by acids or bases and where we can prove the formation of substrate-salt, we assume the substrate-ions to cause the increased reaction velocity, as the substrate-ions are hydrolysed more rapidly than the free substrate molecules. This kind of interacting ion plays of course no rôle, when neutral salts act as catalysts near the point of maximum stability, as e.g. in the catalytic reactions studied by Lowry (*J. Chem. Soc.*, 1927, 2539) and by Brönsted (*J. Am. Chem. Soc.*, 49, 2554, 1927). In these cases we assume that the compounds between the neutral salts and the substrate play the rôle of interacting molecules, existing in a definite concentration and acting with a specific activity higher than that of the free substrate.

$$k = \frac{k_0 + r q_1 \frac{K_a}{h} + r q_2 \frac{K_b}{K_w} \cdot h}{1 + \frac{K_a}{h} + \frac{K_b}{K_w} \cdot h} \quad . . . . . \quad (I)$$

Let us now return to real hydrolyses, for instance to the hydrolyses of carboxyl acid esters, R. CO. O. R<sub>1</sub>. Substrates of this type we consider, as I mentioned above, as amphoteric electrolytes. For such carboxyl esters<sup>6</sup> we find a relation between the reaction constant and  $p_H$  as is seen in Fig. 1. For ethyl acetate this relation is expressed by the formula:—

$$k_{25} = 4 \cdot 10^{-9} + 4 \cdot 27 \times 10^{-14}/h + 2 \cdot 37 \times 10^{-8} \times h.$$

In this way we studied in Stockholm the  $p_H$ - $k$ -curves of about 12 esters, and, within a certain range of acidity, we found analogous curves for the hydrolysis of amides.

The fact that our experimental results can be represented by the formula given above is no proof of our theory. A formula of the type

$$k = k_0 + A/h + B \cdot h$$

accords well with the original view that catalysis is the result of collisions or shocks between the molecules of catalyst and substrate. The theory of shock reactions, as now used by Brönsted in a great number of important papers, differs from the theory of interacting ions, in so far as no equilibrium existence is supposed for the "critical complex," formed at the collision of substrate and catalyst. By such collisions two new molecules are formed and separated in periods corresponding to a revolution of a valency electron.

FIG. 1.—Hydrolysis of carboxyl esters (X Methyl acetate, O Ethyl acetate, Δ Mono-acetin).

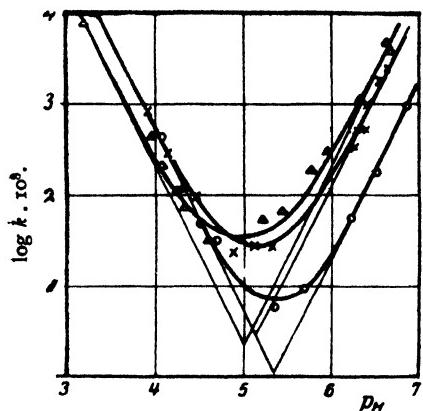
electron.

In opposition to the theory of shock-catalysis we suppose that the interacting ion has a definite average life period and therefore even a definite concentration. If we take as an example the hydrolysis of acetamide we find that the ion  $\text{CH}_3 \cdot \text{CO} \cdot \text{NH}_3^+$  (or its hydrate  $\text{CH}_3 \cdot \text{CO} \cdot \text{NH}_3^+ \cdot \text{H}_2\text{O}$ ) does exist in measurable concentrations in solutions of definite acidity.<sup>7</sup> After a certain period the valency electrons of the group  $-\text{CO} \cdot \text{NH}_3^+$  enter into such labile positions that the splitting of the molecule may take place.

Only in the special case when the splitting velocity  $rq$  of the interacting ion is as large as its formation velocity do the theories of "shock catalysis" and of "interacting ions" lead to an identical conception of catalytical mechanism. The average half life period of the glucosate-ion has been calculated as 0.27 sec. and the corresponding value of the ethyl acetate

<sup>6</sup> It must be emphasised that sulphonic esters, having no amphoteric character, are not hydrolysed by strong acids (Wegscheider, Praetorius, K. G. Karlsson).

<sup>7</sup> Even from the point of view of a shock catalysis one can hardly avoid taking into consideration the specific velocity of such hydrolysable substrate ions, the concentration of which can be quantitatively measured (e.g. the specific reactivity of acetamide cations or of glucosate ions).



anion is approximately 0.1 sec. As these ions are formed by neutralisation their formation velocity must be very much higher.<sup>8</sup>

### Some Consequences of the Hypothesis of Interacting Ions.

In many cases a mathematically correct description of catalysed hydrolysis can be given as well from the standpoint of shock catalysis as from the standpoint of interacting ions. The consequences of both theoretical views seem to be in practical agreement whenever the reaction velocity is proportional to the concentration of the catalysing ions, ( $H$ ) or ( $OH$ ).

However, such a proportionality is by no means general. In fact, whenever a considerable part of the substrate is neutralised by the catalyst the disproportionality must appear (supposing the reaction velocity is not so high that it cannot be measured.)

*Hydrolysis of Acetamide.*—Studying this reaction Ölander and I found that proportionality between the reaction constant  $k$  and  $h$  is out of the question,  $k$  increasing much less than  $h$ . We studied this reaction because in a critical paper Skrabal<sup>9</sup> had claimed the existence of this disproportionality as a consequence of Euler's theory. In fact, this disproportionality does exist and it had been already found in 1907 by Acree and Nirdlinger;<sup>10</sup> but these author's results had been overlooked even in following papers.<sup>11</sup> Recent and exhaustive experiments of Ölander then led to Table I. in which the dissociation constants  $K_b$  of acetamide have been calculated in two ways: (a) with one correction (taking into consideration the dilution of the solution by acetamide (values A)), (b) with two corrections (taking into consideration even the change in activity of the ( $H$ )-ions (values B)).

Thus we found:

		A	B
$K_b$ ( $20^\circ$ )	.. .	$2.5 \cdot 10^{-15}$	$3.8 \cdot 10^{-15}$
$K_b$ ( $50^\circ$ )	.. .	$2.0 \cdot 10^{-14}$	$3.1 \cdot 10^{-14}$

$\gamma$  = rate of dissociation of the amide salt.

TABLE I.

	$n$	$P_H$	$10^4 \cdot k$	$10^4 \cdot k : h$	$\gamma(B)$	$k : \gamma(B)$
1	0.100	1.04	2.93	32.3	0.0386	0.00765
2	0.200	0.76	5.40	31.1	0.0710	0.0076
3	0.300	0.59	7.83	30.5	0.1027	0.0076
4	0.600	0.30	13.40	26.7	0.181	0.0074
5	1.0	0.05	21.35	24.0	0.282	0.0076
6	1.50	- 0.15	29.4	20.8	0.383	0.0077
7	2.00	- 0.30	33.5	16.8	0.457	0.0072
8	2.60	- 0.45	36.2	12.9	0.554	0.0065
9	3.12	- 0.58	37.0	9.7	0.626	0.0059

The fifth column of Table I. shows the decrease of the rate  $k : h$ . Fig. 2 shows that in  $h$  concentrations (from about 1  $N$  HCl)  $k$  is not proportional to, but tends to become independent of  $h$ . From columns 6 and 7

<sup>8</sup> On different grounds we must suppose a very high neutralisation velocity; we know from the interesting experiments of Hartridge and Roughton (*Proc. Roy. Soc., A*, 104, 376, 1923), that the neutralisation period must be less than 0.01 sec.

<sup>9</sup> *Z. Elektroch.*, 33, 322, 1927.

<sup>10</sup> *Am. Chem. Journ.*, 38, 489.

<sup>11</sup> Euler and Rudberg, *Z. anorg. Chem.*, 137, 244, 1923.

we see the ionised part of the acetamide present. The constancy of the rate  $k : \gamma$  must be regarded as very good, considering that  $n$  varies from 0.1 to 3.1.

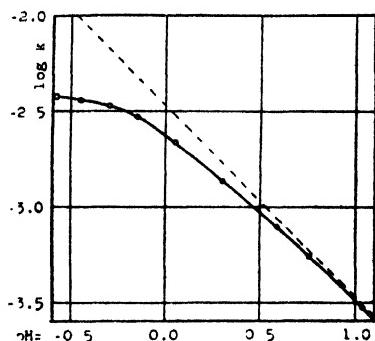


FIG. 2.—Hydrolysis of Acetamide at 50° C.

any other group of the molecule than on one of the groups—CO . NH, where this molecule is hydrolysed into glycylglycine.

We see the kinetic results from Table II.

TABLE II.

$n$ .	$oh.$	$k.$	$\frac{D}{k_d}$
0.05	0.042	0.00515	0.249
0.08	0.068	0.0113	0.247
0.09	0.077	0.0146	0.263
0.10	0.087	0.0160	0.240
0.133	0.118	0.0265	0.258
0.15	0.133	0.0309	0.256
0.20	0.183	0.0440	0.246
0.25	0.230	0.0575	0.250
0.30	0.280	0.068	0.243
0.35	0.327	0.074	0.230
0.40	0.377	0.091	0.252
0.50	0.476	0.110	0.256

The first column indicates the titre of the alkali, the second the average concentration of  $(OH)^-$  during the reaction. If we take the rate  $k/(OH)^-$  the values are not constant, but rather proportional to  $(OH)^-$ . We find that in dilute alkaline solution the reaction velocity is proportional to the square of the catalysing ions. By special experiments it was proved that Na-ions have no part in this effect. We come to the conclusion that it is the double-charged ions of the dioxopiperazine that play the interacting rôle in this catalysis. Therefore in our kinetic formula we must introduce the constants of the primary and of the secondary dissociation.

If  $D$  is the total concentration of dioxopiperazine,

$d$  the concentration of the uncharged molecules,

$d^-$  " " " simple charged molecules,

$d^{--}$  " " " double charged molecules,

we find easily

$$\frac{D}{d^{--}} = \frac{K_w^2}{K_1 \cdot K_2 \cdot oh^2} + \frac{K_w}{K_2 \cdot oh} + 1.$$

This value  $\frac{D}{d^-}$  is used in the fourth column, and it is calculated with the dissociation constants:

$$\frac{K_1}{K_w} = 8. \quad \frac{K_2}{K_w} = 2.$$

As mean value we obtain  $r_{q1} = 0.249$ .

If we plot  $\log k$  against  $\log oh$  we do not obtain, as usual, a straight line with an inclination of  $45^\circ$ , but the curve begins with an inclination of arc  $\operatorname{tg}^2 = 63.5^\circ$ , continues at  $oh = \frac{K_w}{K_1}$  with an inclination of  $45^\circ$ , and ends with an horizontal part from  $oh = \frac{K_w}{K_2}$  (Fig. 3).

Seen from the view of shock catalysis two alternative explanations can be given. One may regard the process either as a bimolecular reaction between  $(\text{OH})$  and  $d^-$  (being forced to take an interacting ion into consideration) or as a termolecular reaction between 2  $(\text{OH})$  and uncharged  $d$ .

### The Reactivity $r_q$ of the Interacting Ions.

From formula (1) we see that we must assume a very much higher reactivity for the interacting ions than for the uncharged free substrate, and it seems natural to ask the reason. The writer need scarcely say that he considers this question as very important in every theory of catalysis. But as no quantitative results are yet obtained I prefer to discuss the interesting views of Böeseken,<sup>12</sup> Lowry,<sup>13</sup> J. W. Baker, Ingold, and Thorpe<sup>14</sup> on another occasion and now to refer only

to the chemical statement (Hantzsch and others) that ionisation generally takes place together with structural transformations and with deformations in the sense of Fajans. We may expect that such deformations should take place to a considerable degree in that group of atoms of a substrate molecule in which the electron or proton is taken up and which is the reactivity-determining part of the molecule.

The problem of catalysis is a chemical one and naturally we have to look for relations between the chemical structure of the substrate and its reaction velocity. Two points I wish to emphasise in this respect.

If we try to find relations between the radicles of a certain kind of substrate, e.g. esters and their reaction velocity, we have to remember that the velocity constant of a catalysed reaction is determinated by two values, namely  $K$  and  $r_q$  (or, if we consider an amphoteric substrate by two pairs of constants, namely  $K_w, K_b, r_{q1}$  and  $r_{q2}$ ). The numerous attempts to find strict relations between the reaction velocity and the constitution of esters have

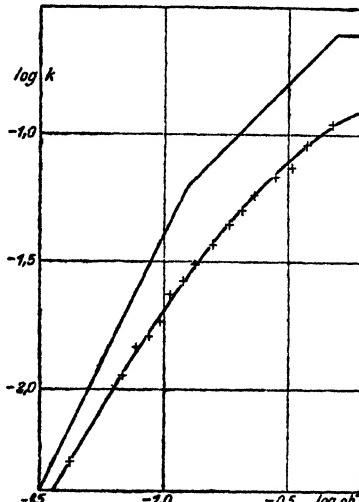


FIG. 3.—Hydrolysis of Dioxopiperazine at  $20^\circ \text{C}$ .

<sup>12</sup> *Chemisch. Weekblad*, 25, 1928.

<sup>13</sup> *Loc. cit.*

<sup>14</sup> *J. Chem. Soc.*, 125, 268, 1924; 1928, 1583.

not led to results of general character, the reaction constant  $k$  itself being of a complex nature.

Using the experimental data for ester hydrolysis of Löwenherz and Hemptinne I compared these velocity constants with the dissociation constants of the corresponding acids.<sup>15</sup> Many exceptions from proportionality were found. Since that time a large amount of experimental material has been collected on the question of structural influences on the velocity constants of ester hydrolysis in acid and, especially, in alkaline solutions (Palooma, Findlay, Skrabal, Smith, H. Olsson, Holmberg, Kindler, and others). Now, we see from our formula

$$k = k_0 + r\gamma_1 \cdot K_a/h + r\gamma_2 \cdot \frac{K_b}{K_w} \cdot h$$

why it is that a proportionality between  $k$  and  $K$  of the acids of the corresponding esters cannot be general. The velocity constant  $k$  is a function of  $K_w$ , the dissociation constant of the ester. We may assume that the electrochemical (negative) character of an acid, measured from its dissociation constant  $K_{acid}$ , should be influenced by any chemical substitution in a similar way as is the negative electrochemical character of the corresponding ester, measured from  $K_{a\ ester}$ . We may expect a simple relation, probably a direct proportionality, between  $K_{acid}$  and  $K_{a\ ester}$  thus

$$\frac{K_{acid}}{K_{a\ ester}} = const.$$

If we compare the saponification velocities  $k$  and  $k'$  of two ethyl esters of two different acids at such an alkalinity that  $k$  and  $k'$  are proportional to  $(OH)$  we may neglect the terms  $k_0$  and  $r\gamma_2 \cdot \frac{K_b}{K_w} \cdot h$  and we find

$$k : k' = K_a : K'_a = K_{acid} : K'_{acid}.$$

This simple relation will, however, hold *only* if  $r\gamma$  is constant.<sup>16</sup>

Every substitution influencing the structure of the reacting group, the relative distance of its atoms and at the same time the molecular volume, will also influence the specific reactivity  $r\gamma$ . If it should be possible to eliminate this influence of  $r\gamma$ , the connection between  $k$  and  $K_{a\ ester}$  claimed by the theory, would appear more clearly.

Having no data on the electro-affinity of the radical R. CO<sup>-</sup>, we do not know if we can expect analogous simple reactions between the velocity constants of acid hydrolysis of esters and the dissociation constants of their acids.

If we wish to clear up the total reactivity of the esters, we must study the whole  $\rho_H$  curve of reaction velocity and in this way fix the maximum of stability of the esters, as was done by K. G. Karlsson<sup>17</sup> and by I. Bolin.<sup>18</sup> As mentioned above the condition of this maximum point is  $K_a \cdot r\gamma_1 \cdot OH = K_b \cdot r\gamma_2 \cdot h$ , but it seems that this point is influenced in the first place by the ratio  $K_a/K_b$ .

The following values, partly taken from a recent paper of I. Bolin,<sup>19</sup> show the considerable variations in the  $\rho_H$ -stability of different esters.

<sup>15</sup> Z. physik. Chem., 1901, 36, 405.

<sup>16</sup> Compare the results of H. Olsson, Z. physik. Chem., 133, 233, 1928.

<sup>17</sup> Z. anorg. Chem., 119, 68, 1921; 145, 1, 1925.

<sup>18</sup> Ibid., 143, 201, 1925.

<sup>19</sup> Ibid., 1928.

Ester.		$p_{H^+}$	Temp.
Ethyl ester of formic acid . . . . .		4·65	20°
" " acetic " . . . . .		5·36	25°
		5·1	70°
" " butyric " . . . . .		5·65	25°
" " monochlor-acetic acid . . . . .		4·8	20°
" " phenylacetic acid . . . . .		4·9	25°
" " aceto-acetic " . . . . .		4·4	25°
" " amino-acetic " . . . . .		3·8	20°
" " chlor-propionic acid . . . . .		4·0	25°
" " benzoic acid . . . . .		4·15	80°
" " hippuric " . . . . .		4·4	25°
Methyl ester of acetic " . . . . .		5·15	25°
" " benzoic acid . . . . .		4·0	80°
Phenyl ester of acetic acid . . . . .		4·1	25°
Benzyl " " . . . . .		4·3	25°
Glyceryl ester of acetic acid (monacetine) .		5·0	25°

### Interacting Compounds between Substrates and Catalysts in Enzyme Chemistry.

There is a large group of catalytic reactions in which the hypothesis of interacting compounds between substrate and catalyst has led to many and important consequences and has been generally adopted for many years. In enzyme chemistry this view was put forward by Kastle and Loevenhart, by E. F. Armstrong and by V. Henri, and has been developed to a quantitative theory by Michaelis, 1913.

Readers who are not familiar with the kinetics of enzyme action will perhaps doubt the existence of a real analogy between enzymatic and non-enzymatic catalysis. Indeed, with regard to the groups combining the substrate with the enzyme we have a definite knowledge only in one case: *the NH<sub>2</sub>-group of the dipeptides*, linking the dipeptidase to its substrate.<sup>20</sup> But thinking that the detailed pursuit of the analogy between enzymatic and non-enzymatic catalysis will become fertile for both parts of catalytic research and for chemical kinetics in general, I wish to illustrate it by some data.

Michaelis in his fundamental work, 1913, indicated a method of calculating the affinity between a substrate and an enzyme. I am going to give a similar but somewhat simpler deduction taking as example the system sugar-saccharase.

According to the law of mass action the affinity constant  $K_M$  is expressed by the formula, in which [ ] designs the concentrations:—

$$K_M = \frac{[\text{enzyme} - \text{substrate}]}{[\text{enzyme}] \times [\text{substrate}]}.$$

We know the concentration of the substrate in the reacting solution but not the absolute concentration of the enzyme.

In enzyme reactions the monomolecular constant  $k$  is generally not independent of the concentration of the substrate. If we start from a solution containing a certain quantity of enzyme and if we measure the reaction velocity with increasing quantity of sugar, the rate of sugar inverted per minute increases and reaches a maximum value (Fig. 4).

<sup>20</sup> Euler and Josephson, *Z. physiol. Chem.*, 157, 122, 1926; 166, 294, 1927; *Chem. Ber.*, 60, 1341, 1927; Waldschmidt-Leitz and co-workers, *Chem. Ber.*, 60, 359, 1927; Grassmann and Dyckerhoff, *Z. physiol. Chem.*, 175, 18, 1928.

We suppose that at the point where this maximum is reached the total quantity of enzyme is combined with the sugar. A further excess of sugar therefore cannot take part in the reaction. By interpolation we can determine the sugar concentration, when the reaction velocity is one half of the maximal velocity. At this point half of the enzyme is combined with the sugar, the rest of the enzyme is free, and at this point the concentrations of free enzyme and of compound enzyme-substrate are equal. From the above equation we can calculate  $K_M$  as the inverse value of the substrate concentration, at which one half of the maximum reaction velocity is observed. In this way we obtain for a certain type of saccharases  $K_M = 50$ .

Using this saccharase I have recently made new comparative experiments together with Ölander<sup>21</sup> and Josephson.<sup>22</sup>

Approximating the molecular weight of our enzyme to 20,000 we calculate for a solution reacting with a certain velocity ( $k = 83 \cdot 10^{-4}$ ) the concentration of the interacting molecules enzyme-substrate, and we find from this value the specific reactivity,  $r\gamma$  being about  $5 \cdot 10^5$ .

As regards the non-enzymatic inversion of cane-sugar by a strong acid, we can calculate the rate of combination between acid and sugar according to the law of salt hydrolysis, the sugar acting as a weak base.<sup>23</sup>

For such a calculation we must make an approximation concerning the dissociation constant  $K_b$  of the sugar ( $K_b \sim 10^{-20}$ ), leading thereby to an un-

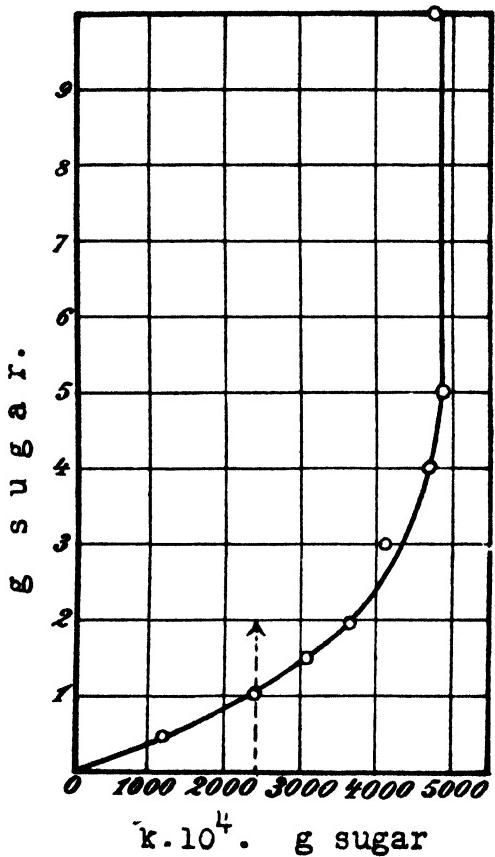


FIG. 4.—Inversion of sugar.

certainty of several powers. In this way we find for the interacting sugar ion the value  $r\gamma_2 = 4 \cdot 10^3$ .

If we compare an enzymatic and a non-enzymatic solution hydrolysing the same quantity of sugar with the same velocity, we find that the concen-

<sup>21</sup> Z. anorg. Chem., 156, 143, 1926.

<sup>22</sup> Cf. for instance, Euler, Chémie d. Enzyme, 3rd edition, II., 1 (1928), p. 189.

<sup>23</sup> If we regard the equilibrium between substrate and catalysing acid as a hydrolysis equilibrium, we accept the theoretical view of "dual catalysis" (Dawson, Senter, Snethlage, and others) as a consequence, according to the principles of the dissociation theory and of the law of mass action.

trations of the interacting molecules sugar-enzyme on the one hand and sugar-acid on the other, are of a similar order of magnitude and that even the specific reactivities  $rq$  of both kinds of interacting molecules are not very different.

In enzymatic catalysis we have the catalyst in small concentration, combined with the substrate by a high affinity constant; in catalysis by strong acids and bases the catalyst concentration needed is about a million times higher,<sup>24</sup> and at the same time the affinity constant of this compound is about a million times smaller.

The result, *viz.*, that the specific reactivity of the interacting molecules in both cases is similar, leads to the assumption that the reacting part of the substrate is in both cases changed in a similar manner as regards the structure; we may imagine that by addition of the catalyst the distance between the two groups of the hydrolysable substrate has been increased.<sup>25</sup>

### Summary.

In this contribution to the discussion on Homogeneous Catalysis I have tried to give the main features of the theory of interacting ions, as far as catalytic hydrolysis by acids or bases is regarded.

The assumption of intermediate compounds between substrate and catalyst has often been used for qualitative explanations of catalytic processes since the middle of the last century. The more special theory here presented leads to expressions containing two (or in cases of amphoteric substrates two pairs of) constants, the dissociation constant  $K$  and the specific reactivity  $rq$ . In a number of reactions the above dissociation constants have been measured and the values of  $rq$  have been calculated from them. In this combination of the reaction velocity with other determinable constants I see the advantage of this theory. While the theory of shock catalysis can not predict which molecule will be split by the collision with an  $H^+$  or an  $OH^-$  ion and under what circumstances such a collision will be successful, we have in our theory the chemical criteria for the possibility of salt formation between substrate and acid or base.

The quantitative proof of this theory is in many cases difficult, because the dissociation constants  $K_a$  or  $K_b$  of the substrates are so small, and the present methods, giving only dissociation constants up to  $k = 10^{-15}$  are insufficient. Assuming in these cases the existence of very small dissociation constants we make no *ad hoc* hypothesis, but rely entirely upon our knowledge of the connection between constitution and electrochemical character. Hitherto no case has been found in which the supposition of salt formation between substrate and acid or basic catalysis contradicts chemical experience.

On the other hand, our method of treating catalytic problems is in a state of development and has to be worked out in different directions. We need, for instance, data for the concentration of intermediate compounds between substrates and neutral salts under different conditions. Particularly we need much more material with regard to the relation between the reactivity of substrate ions and their chemical constitution and the transformations accompanying ionisation of a substrate. Our theory will give more correct interpretation when we are able to calculate in advance the reactivities  $rq$  from other static or dynamic constants of the substrate

<sup>24</sup> Euler and Ölander, *Z. anorg. Chem.*, 156; Euler, *Chem. Ber.*, 55, 3583, 1922.

<sup>25</sup> Euler, *Sv. Vet. Akad., Arkiv f. Kemi*, 9, 30, 1926.

molecules and ions. In any case our knowledge of chemical kinetics and of the mechanism of catalysis will be enlarged by research on the reactivity of substrate ions and consequently by the experimental determination of the values  $r\eta$ .

## ON THE CATALYTIC ACTIVITY OF HYDROGEN IONS IN ETHYL ALCOHOL.

BY HEINRICH GOLDSCHMIDT.

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When in the year 1895 I commenced the study of the catalytic effect of strong acids on the formation of esters with alcohols, I was of opinion that the hydrogen ions of strong acids might be the catalysts. I assumed that the velocity of ester formation was proportional to the concentration of the hydrogen ions. I was later led to the conclusion, as a result of the study of the anticatalytic effect of the addition of water to the alcohols, that the hydrogen ions do not react as such in this case but as additive products with the alcohol, the complex ions [Alcohol-H<sup>+</sup>]. I concluded, however, that the effect was proportional to concentration. As a result of my studies with catalysis when weak acids, such as picric acid or trichlorobutyric acid, are used, I was forced to the conclusion that the undissociated addition products of the alcohol and the catalyst acid (such as, for example, C<sub>2</sub>H<sub>6</sub>O · C<sub>4</sub>H<sub>5</sub>Cl<sub>3</sub>O<sub>2</sub>) must play a part in producing the catalytic effect as well as the complex ion above-mentioned; I followed the progress of ester formation in methyl alcohol<sup>1</sup> and in ethyl alcohol<sup>2</sup> by calculating, according to the formula  $\frac{A_v}{A_\infty}$ , the degree of dissociation of the catalyst as shown by conductivity determinations. Later on, when the new views on electrolytic dissociation were developed, I calculated the degree of dissociation  $\alpha$  of different acids in methyl alcohol by Bjerrum's method and, with the help of these figures, derived the velocity constant  $K$  for unit concentration of hydrogen ions, corresponding to the addition product, by means of the formula

$$K = \frac{k}{\alpha},$$

where  $k$  is the velocity constant for a concentration  $c$  of the catalyst, the reaction being considered as unimolecular. If the measure of hydrogen ions or complex ions were dependent on concentration alone,  $K$  should be of the same dimensions when different catalyst acids were used, and even a variation of  $c$  should be without influence.

Experiments with methyl alcohol proved that when picric acid, trinitro-*m*-cresol, trichloroacetic acid, and trichlorobutyric acid were used,  $K$  was in fact of approximately the same dimensions and, also, that variation of  $c$  had only a slight influence. Tables containing these results will be found in the original papers in *Z. physikal. Chem.*, 117, 312, and 129, 223.

When I approached in an analogous manner, by Bjerrum's method, the degree of dissociation, calculated by E. Larsson from my figures and those of my pupils, for conductivity in ethyl alcohol solution, relating it to our

<sup>1</sup> *Z. physik. Chem.*, 81, 30, 1912.

<sup>2</sup> *Ibid.*, 94, 223, 1920.

velocity measurements in ethyl alcohol, I no longer found the same agreement as in methyl alcohol, but the values of  $K$  varied very greatly. The weaker the catalyst used, the larger was the value of  $K$ , and for one and the same acid  $K$  became smaller if the catalysing acid were used in low concentrations. Table I. gives the figures for the combination of the four acids, acetic, phenyl acetic, *n*-butyric, and *iso*-valeric, with the four above-mentioned catalysing acids.

TABLE I.

Catalyst.	$c$ .	$a$ .	$C_2H_4O_2$ .		$C_6H_5C_2H_5O_2$ .		$n.C_4H_8O$ .		$iso\ C_6H_{10}O_2$ .	
			$k$ .	$K$ .	$k$ .	$K$ .	$k$ .	$K$ .	$k$ .	$K$ .
$C_6H_2(NO_2)_3O$	0.1	0.0612	0.1640	26.8	0.0680	11.2	0.0610	10.0	0.0136	2.22
"	0.05	0.0765	0.1035	27.1	0.0433	11.3	0.0401	10.5	0.00855	2.24
$C_7H_5(NO_2)_3O$	0.1	0.138	0.0370	26.8	0.0550	10.9	0.0141	10.2	0.00295	2.14
"	0.05	0.0255	0.0371	29.9	0.0228	12.1	0.0216	11.4	0.00493	2.61
"	0.01	0.0515	0.0148	28.7	0.00590	12.0	0.0144	11.3	0.00321	2.52
$C_2HCl_3O_2$	0.1	0.0046	0.0161	35.0	0.00712	15.5	0.00670	14.5	0.00162	3.52
"	0.05	0.0062	0.0101	32.6	—	—	—	—	—	—
$C_4H_6Cl_3O_2$	0.1	0.001108	0.00420	37.9	0.00204	18.5	0.00183	16.5	0.000467	4.21
"	0.05	0.001536	0.00268	34.9	0.00126	16.4	0.00113	14.7	0.000287	3.74

From this table the following deductions may be made :—

(1) The values of  $K$  increase continuously from picric acid, the strongest acid, to trichlorobutyric acid, the weakest.

(2) The values of  $K$  obtained with picric acid show well that they are independent of the concentration of this acid. When, however, trinitro-cresol was used it is seen that the fall in the value of  $K$  is becoming apparent, and in the case of trichloroacetic and more especially trichlorobutyric acid this decrease in the value of  $K$  is very noticeable with every acid used.

Both phenomena lead us to the conclusion that the hydrogen ions, or, more correctly their alcohol addition products, are not the sole catalysts. We are therefore forced to the conclusion that we must ascribe a catalytic effect to the undissociated acid, or, more correctly to its addition product with alcohol. Taking trichlorobutyric acid as example, the addition product  $C_2H_6O \cdot C_4H_5Cl_3O_2$  exercises a catalytic effect as well as the ion  $C_2H_6O \cdot H^+$ . We can no longer write

$$K = \frac{k}{ac},$$

but we must introduce two characteristic constants for each acid used for esterification,  $K_H$  for the effect of the hydrogen ion,  $K_S$  for the effect of the undissociated catalysing acid. The value of  $K_H$  is the same for all catalysts so long as the same acid is used for esterification, whilst  $K_S$  varies with the catalyst and also with the acid used for esterification. The velocity of reaction  $k$  is made up as follows :

$$k = acK_H + c(1 - a)K_S.$$

If now we continue the  $K$  values for one and the same catalyst acid and esterifying acid for two different concentrations  $c$  and if we fix the corresponding  $a$  values which are given by my conductivity measurements, we can evaluate  $K_H$  and  $K_S$ .

The values in Table II. were derived from experiments with 0.1 and 0.05*N* trichlorobutyric acid and 0.1 and 0.01*N* trinitro-*m*-cresol.

TABLE II.

Acid.	$C_4H_5Cl_3O_2$ .		$C_7H_5N_3O_7$ .	
	$K_H$ .	$K_S$ .	$K_H$ .	$K_S$ .
Acetic . . .	27.3	0.0119	28.1	0.0348
Phenylacetic . .	10.9	0.00863	11.1	0.0177
<i>n</i> -Butyric . .	9.8	0.00747	10.6	0.0160
<i>iso</i> -Valeric . .	2.5	0.00192	2.3	0.0066

The figures for  $K_H$  given in this table agree fairly well with the figures for  $K$  given in Table I. for picric acid. In the case of this acid, which is comparatively strongly dissociated, the influence of the undissociated acid must vanish in comparison with that of the hydrogen ions and therefore  $K$  proves to be independent of concentration. With the other catalysing acids, which are less dissociated, we take into consideration  $K_S(1 - a)$  as well as  $K_{Ha}$ . These  $K_S$  values are of different magnitudes for the different combinations of catalyst acid and esterifying acid, since they relate to processes of different types.

As to  $K_S$  there is still one characteristic to which attention should be drawn but which is difficult to understand. One would expect that with an acid so weak, in ethyl alcohol solution, as trichlorobutyric acid (affinity constant  $8.4 \times 10^{-8}$ ) by addition of sodium salts the electrolytic dissociation would be restrained to such an extent that the velocity constant would equal or at any rate approach  $c \times K_S$ . Now we have estimated the velocity of esterification for all four acids with a mixture of 0.1*N* trichlorobutyric acid and 0.1*N* sodium trichlorobutyrate, and the velocity constant  $k_{salt}$  proves in every case to be much smaller and not, as we had expected, somewhat larger than  $K_S$ , as may be seen from Table III. Possibly the alteration of viscosity caused by the salt addition may be one of the causes of this unexpected result.

TABLE III.

Acid.	$K_S c$ .	$k_{salt}$ .	$\frac{k_{0.1}}{k_{salt}}$ .
Acetic . . .	0.000119	0.000060	7.0
Phenylacetic . .	0.000863	0.000478	4.27
<i>n</i> -Butyric . .	0.000747	0.000346	5.3
<i>iso</i> -Valeric . .	0.000192	0.000129	3.62

The figures in the last column give the relation of the velocity constant, with 0.1*N* trichlorobutyric acid (see Table I.) as catalyst without 0.1*N* addition of salt, to that with the addition. The hydrogen ion concentration in such a mixture of free acid and salt must always be the same. Since the decrease of the velocity is of a different magnitude with different acids it cannot be the hydrogen ion alone which catalyses the reaction, but there

must be another factor. It seems to me that the most obvious explanation is again that the undissociated part of the acid behaves as catalyst.

A further observation might here be made which shows a difference between the catalytic effects of picric acid and the weaker acids and which should serve to make very clear a more marked effect of the undissociated part of the weak acids. Twelve years ago Bjerrum put forward the following formula on the result of my experiments with picric acid catalysis in ester formation in methyl alcohol :

$$\kappa = \frac{k}{K} \frac{b}{a} f^2$$

wherein  $\kappa$  is the affinity constant of picric acid in ethyl alcohol ( $8.3 \times 10^{-5}$ ),  $k$  the observed velocity constant,  $K$  the constant for the hydrogen ion concentration  $i$ ,  $a$  the concentration of picric acid,  $b$  that of the added picrates, and  $f$  the activity coefficient. The hydrogen ion concentration is given by  $\frac{k}{K}$ . As a result of a large number of experiments with a large range of acids (acetic, formic, phenylacetic, *n*- and *iso*-butyric and others), moreover under greatly varying conditions of  $a$  and of  $b$ , it follows that  $f$ , the activity coefficient, is practically the same for all acids and for all possible concentrations of picric acid ( $a$ ), provided that  $b$ , the salt addition, is kept constant. If  $b$  is increased  $f$  is diminished and if  $b$  is diminished  $f$  is increased, and these variations are practically independent of the nature of the acid and of the magnitude of  $a$ . In Table IV. the values of  $f$  are given for the three acids (acetic, phenylacetic and *n*-butyric); aniline picrate was used as the salt.

TABLE IV.

<i>a.</i>	<i>b.</i>	Acetic acid $K = 27.1$ .		Phenylacetic acid $K = 11.1$ .		<i>n</i> -Butyric acid $K = 9.5$ .	
		<i>k.</i>	<i>f.</i>	<i>k.</i>	<i>f.</i>	<i>k.</i>	<i>f.</i>
0.1	0.025	0.0899	0.315	0.0367	0.313	—	—
0.05	0.025	0.0458	0.312	0.0188	0.310	—	—
0.1	0.05	0.0736	0.246	—	—	—	—
0.05	0.05	0.0374	0.245	0.0152	0.244	0.0145	0.246
0.01	0.05	0.00734	0.246	0.00325	0.237	—	—
0.1	0.1	0.0548	0.196	0.0242	0.193	0.0235	0.193
0.05	0.1	0.0301	0.195	0.0125	0.190	—	—
0.01	0.1	0.00570	0.196	0.00239	0.194	0.00231	0.193

The constancy of the values of  $f$  and their dependence on  $b$  alone stands out clearly. It still remains to prove that  $f$  as shown in the above experiments is actually the activity coefficient, and this is only possible if  $\frac{k}{K}$  corresponds to the hydrogen ion concentration. The activity of picric acid in alcoholic solution in the presence of sodium picrate has been potentiometrically estimated by E. Larsson with the aid of quinhydrone electrode. As Larsson himself admits, such experiments are difficult and the results are therefore slightly affected by errors. Nevertheless the agreement between Larsson's  $a_H$  values and the product  $\frac{k}{K}f$  is sufficiently perceptible, as is to be seen in Table V.

TABLE V.

$a.$	$b.$	$a_{H^+}$	$\frac{k}{K}f$
0.05	0.025	0.00036	0.00035
0.1	0.025	0.00098	0.00106
0.05	0.05	0.00068	0.00053
0.1	0.05	0.00083	0.00067

One may conclude from these results that the concentration of the catalytically effective hydrogen ions is given by the expression  $\frac{k}{K}f$ , and there is no room left for a catalytic effect by the undissociated part of the picric acid.

As soon, however, as we turn to trichlorobutyric acid we are faced with different circumstances. If we carry out the same calculation for trichlorobutyric acid plus sodium salt, as was used for picric acid plus picrate, by combining with the figures given in Table III. for the value of  $k$ , the value of  $\kappa$  for trichlorobutyric acid ( $8.3 \times 10^{-8}$ )<sup>salt</sup>, we find no longer an agreement between the values of  $f$  for the different acids, independently of whether we take the value for  $K$  from Table I. or that for  $K_H$  from Table II.

By still other examples, we are brought to the conclusion that the hydrogen ion concentration is not the only decisive factor for the catalytic effect of acids in ethyl alcohol. For the present I am content to set forth this portion of my work. Perhaps it succeeds in giving, by the application of the newer view-point of electrolytic dissociation, a better explanation of the observations here set forth.

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## INVESTIGATIONS OF SALT ACTION IN HOMOGENEOUS CATALYSIS.

BY HERBERT S. HARNE AND GÖSTA ÅKERLÖF.

*Received 16th July, 1928.*

If we consider a reaction between the substances A, B, etc., we may express the velocity by the equation

$$v = k' c_A c_B \dots F, \quad \dots \quad \dots \quad \dots \quad (1)$$

and denote  $F$  the "kinetic factor." In case A, B, etc. are neutral substances and the solution is neutral,  $F$  equals unity as a first approximation. In ionic solutions, or when A or B, etc., or A and B, etc., are ions,  $F$  may no longer equal unity, since, if this were the case, it would be impossible to obtain the thermodynamic equilibrium law of many reactions by consideration of the process and its reverse process.

To overcome this difficulty, it has been suggested that part of the

kinetic factor will contain the product of the activity coefficients of A, B, etc. Thus,

$$v = k' c_A c_B \cdots \gamma_A \gamma_B \cdots F'. \quad \dots \quad \dots \quad (2)$$

In order that this equation be consistent with thermodynamics, it is necessary that  $F'$  have the same value for the reaction as for its reverse. When  $F'$  equals unity, we have the "activity rate theory."

The most important advance in the interpretation of  $F'$  has been made by Brönsted<sup>1</sup> who employs the equation

$$v = k' c_A c_B \cdots \gamma_A \gamma_B \cdots \frac{F''}{\gamma_t}, \quad \dots \quad \dots \quad (3)$$

where  $F''$  is taken to be unity,  $\gamma_t$  the activity coefficient of a hypothetical intermediate of extremely short life, and  $\frac{F''}{\gamma_t}$  or  $F'$  is the same for the reaction as for its reverse.

The kinetic factor,  $F$ , may be called "the salt effect," since for the most part it is caused to deviate from unity by the attractive and repulsive electrical forces of the ions. Since to a large extent the activity coefficient is a gross measure of a similar deviation, it is not strange to find that  $F$  is composed of both products and ratios of activity coefficients.

Following Brönsted, we shall recognise two possible effects of salt addition. The primary salt effect is the influence of the addition of salt on  $F$ . The secondary salt effect is the influence of salt addition upon  $c_A c_B \cdots$ , or, more particularly, the influence of salt addition upon the concentration of the catalytic ion.

### Critique of the Above Expressions for the Rate of Homogeneous Reactions Catalysed by Ions.

In our earlier work on salt effects on reactions catalysed by hydrogen, hydroxyl, and iodide ions, an attempt was made to determine whether the salt effect was a function of the individual ion activity coefficient of the catalysing ion.<sup>2</sup> This attempt we regard as a failure because of the peculiarly arbitrary nature of the definition of an individual ion activity coefficient. It appears that no measurement of cells with or without transference can possibly yield any information regarding individual ion activity coefficients.<sup>3</sup> Although the definitions of individual ion activity coefficients as employed by MacInnes and Harned<sup>4</sup> have proved useful in some thermodynamical computations, they can lead nowhere in solving the theoretical problems of a homogeneous ionic solution. We must therefore conclude that when dealing with the problems of homogeneous catalysis only the use of activity coefficient products and ratios of these products may be expected to prove fruitful.

The equation of Brönsted has been found to predict remarkably well the behaviours of many reactions in very dilute solutions. Under this circumstance, however, the values for the individual ion activity coefficients of the catalysing ion and the intermediate are taken to be equal to the mean activity coefficients as given by the theory of Debye and Hückel.

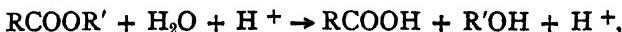
<sup>1</sup> Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); **115**, 337 (1925).

<sup>2</sup> Harned, *J. Amer. Chem. Soc.*, **37**, 2460 (1915); Harned and Pfanstiel, *ibid.*, **44**, 2193 (1922); Åkerlöf, *Z. physik. Chem.*, **98**, 260 (1921); *J. Amer. Chem. Soc.*, **40**, 3046 (1918).

<sup>3</sup> Harned, *J. physical Chem.*, **30**, 433 (1926); Taylor, *ibid.*, **31**, 1478 (1927).

<sup>4</sup> MacInnes, *J. Amer. Chem. Soc.*, **41**, 1086 (1919); Harned, *ibid.*, **42**, 1808 (1920).

Thus, if we consider the hydrolysis of an ester catalysed by hydrochloric acid according to the scheme



we write by the use of equation (3)

$$\overrightarrow{v} = k' c_E c_{\text{H}_2\text{O}} \gamma_E \gamma_{\text{H}_2\text{O}} \left( \frac{\gamma_{\text{H}}}{\gamma_i} \right), \quad . \quad . \quad . \quad (4)$$

where the intermediate is a positive ion. The same result would be obtained in the cases of the dilute solutions had we written  $\sqrt{\gamma_{\text{H}} \gamma_{\text{Cl}}}$  or  $\sqrt{\gamma_i \gamma_{\text{Cl}}}$  for  $\gamma_{\text{H}}$  and  $\gamma_i$ , respectively.

With this general consideration in mind, it is not strange that no quantitative result was obtained when attempting to employ individual ion activity coefficients to account for the kinetic salt effects. On the other hand, some progress has been made by means of activity coefficient products<sup>5</sup> as witnessed by the investigations of Harned and Seltz, and Soper on the hydrochloric acid catalysis of chloroacetanilide, the work of Livingston on the hydrobromic acid catalysis of hydrogen peroxide, and of Åkerlöf on the hydroxide decomposition of diacetone alcohol.

### The Elimination of the Primary Salt Effect in Weak Acid or Weak Base Catalysis and the Calculation of the Secondary Salt Effect.

Suppose we consider the equation for the velocity of the neutral salt catalysis of an ester, namely,

$$v = k' c_E c_{\text{H}_2\text{O}} f(\gamma_E, \gamma_{\text{H}_2\text{O}}, \gamma_{\text{H}}, \gamma_i, \dots), \quad . \quad . \quad . \quad (5)$$

where we have written a general function of the gammas rather than some particular function. The observed monomolecular velocity constant,  $k$ , will therefore be given by

$$k = k' c_{\text{H}_2\text{O}} f(\gamma_E, \gamma_{\text{H}}, \gamma_{\text{H}_2\text{O}}, \gamma_i, \dots). \quad . \quad . \quad . \quad (5a)$$

Let the reaction be catalysed by a strong acid of not too high a concentration (e.g. 0.001-0.01M HCl), then

$$k_s = k' c_{\text{H}(s)} c_{\text{H}_2\text{O}} f(\gamma_s), \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where the subscript "s" refers to the strong acid catalyst. Then let the reaction be catalysed by a weak univalent acid, the hydrogen ion concentration of which is the same or nearly the same as that of the strong acid. Then the velocity constant will be given by

$$k_w = k' c_{\text{H}(w)} c_{\text{H}_2\text{O}} f(\gamma_w), \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where the subscript "w" refers to the weak acid catalysis. The ratio of these two equations gives

$$\frac{k_s}{k_w} = \frac{c_{\text{H}(s)}}{c_{\text{H}(w)}}. \quad . \quad (8)$$

<sup>5</sup> Harned and Seltz, *J. Amer. Chem. Soc.*, 44, 1475 (1922); Soper, *J. Chem. Soc.*, 2761 (1927); Livingston, *J. Amer. Chem. Soc.*, 48, 53 (1926); Åkerlöf, *ibid.*, 49, 2955 (1927).

This equation will be exact in dilute solutions of the pure acids when the hydrogen ion concentrations of the strong and the weak acids are the same. Thus, since we may regard dilute hydrochloric acid as completely dissociated, we know  $c_{H(s)}$ . Then by adjusting  $c_{H(s)}$  until  $\frac{k_s}{k_w}$  equals unity,  $c_{H(w)}$  is obtained. Upon salt addition, however,  $c_{H(s)}$ , the molal concentration of the hydrogen ion, will remain unchanged, but  $c_{H(w)}$  will vary, due to the secondary salt effect on the hydrogen ion concentration of the weak acid. If the reaction velocity constants,  $k_s$  and  $k_w$ , are taken at the same salt concentration,  $c_s$ , so that  $c_s + c_{H(w)} = c_s + c_{H(s)}$ , then equation (8) holds accurately and  $c_{H(w)}$  or the molal concentration of the hydrogen ion in the weak acid solution in the presence of the salts will be known. By this device, the primary salt effect may be eliminated and the secondary effect of the salt on the dissociation of the weak acid be determined.<sup>6</sup>

From the knowledge of the effect of salt addition upon the dissociation of the weak electrolyte, the activity coefficient of the weak acid in the salt solution relative to its activity coefficient at zero salt concentration may be computed by the thermodynamic equation

$$K_a = \frac{\gamma_H \gamma_{Ac}}{\gamma_{HAc}} \cdot \frac{c_H^2}{m - c_H} = \gamma^2 K_e \quad . \quad . \quad . \quad (9)$$

where  $\gamma^2$  equals  $\frac{\gamma_H \gamma_{Ac}}{\gamma_{HAc}}$ ,  $K_e$  is the classic dissociation constant of the acid, and  $m$  its molality.  $K_e$  equals  $K_a$  when the ionic strength equals zero. It is important to note that

$$\gamma = \sqrt{\frac{\gamma_H \gamma_{Ac}}{\gamma_{HAc}}} = \sqrt{\frac{\frac{a_H a_{Ac}}{c_H c_{Ac}}}{\frac{a_{HAc}}{m - c_H}}}$$

where  $c_H$  and  $c_{Ac}$  are the true concentrations of the hydrogen and acid anion. Because of this,  $\sqrt{\gamma_H \gamma_{Ac}}$  will be of the same order of magnitude as that found for the activity coefficients of the completely dissociated strong electrolytes.

Since the activity coefficient of a strong acid first decreases, then passes through a minimum, and then increases upon increase of the ionic strength, whether this increase be brought about by increasing its concentration or by salt addition, we may predict the nature of the secondary salt effect by equation (9). We may expect that upon the addition of salt to a weak acid solution of low hydrogen ion concentration, the hydrogen ion concentration will first increase, then pass through a maximum, and finally decrease. There are available three independent sources of evidence which show that this is unquestionably true:—

(1) Electromotive force determinations upon suitable cells prove that the dissociation of water in salt solutions shows this behaviour.<sup>7</sup>

<sup>6</sup> Brönsted, *J. Chem. Soc.*, **119**, 574 (1921); Brönsted and King, *J. Amer. Chem. Soc.*, **42**, 2523 (1925); Harned, *ibid.*, **49**, 1 (1927); Harned and Hawkins, *ibid.*, **50**, 85 (1928).

<sup>7</sup> Harned, *J. Amer. Chem. Soc.*, **47**, 930 (1925); Harned and Swindells, *J. Amer. Chem. Soc.*, **48**, 126 (1926); Åkerlöf, *ibid.*, **48**, 1160 (1926); Harned and James, *J. physical Chem.*, **30**, 1060 (1926).

(2) Recent measurements of suitable cells without transference give a method of determining the ionic activity coefficient of weak acids and bases in salt solutions as well as their dissociation. Similar behaviours have been observed.<sup>8</sup>

(3) Calculations of kinetic data according to equations (8) and (9) have shown that the same behaviour is observable in the cases of mono- and di-chloro acetic acids.

To illustrate the uniformity of the results obtained by the different methods, we plot in Fig. 1 the ionic activity coefficients of acetic, mono- and di-chloro acetic acids and water in sodium chloride solutions. The values for acetic acid and water were obtained from electromotive force data, and those of the mono- and di-chloro acetic acids from kinetic data.<sup>9</sup> It appears that in a given salt solution  $\gamma$  becomes less with increasing chlorine substitution of acetic acid.

When we come to consider the distribution of the ionic activity coefficients of the weak electrolytes in different salt solutions, we have found

no exception to the following rule: The ionic activity coefficient of a weak acid or base is less at a given ionic strength in a solution of that salt of a given valence type which has the higher activity coefficient in aqueous solution. Reciprocally, the dissociation of the weak electrolyte is greater in the solution of that salt which has the higher activity coefficient.

At this point we wish to emphasise the importance of the secondary salt effect in weak acid and hydroxide catalysis. In the numerous

Fig. 1.—Curves for the ionic activity coefficients of acetic acid (curve I.), monochloroacetic acid (curve II.), dichloroacetic acid (curve III.), and water (dashed curve) in sodium chloride solutions.

recent investigations of Dawson and his collaborator,<sup>10</sup> the rôle of the activity coefficients in determining the secondary salt effect on the concentration of the hydrogen or hydroxyl ion has been omitted. The method of attack outlined above seems to be so promising and to be substantiated by data from so many sources that it is difficult to see how it can be disregarded.

### The Primary Salt Effect in General.

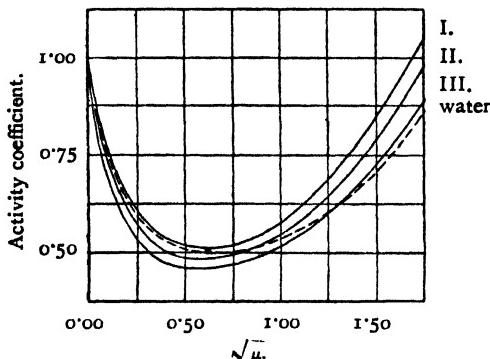
The equation of Brönsted, which, from the statistical considerations of Christiansen,<sup>11</sup> appears to be sound as the limiting case and which predicts very well the valence effects for reactions between ions of various kinds in dilute solutions, will serve as a starting point in a discussion of the primary

<sup>8</sup> Unpublished results obtained by Mr. Robert Robinson.

<sup>9</sup> Harned and Hawkins, *loc. cit.*, n. 6.

<sup>10</sup> Dawson and collaborators, numerous contributions on "Acid and Salt Effects on Homogeneous Catalysis," *J. Chem. Soc.*, 1926 onwards.

<sup>11</sup> Christiansen, *Z. physik. Chem.*, **113**, 35 (1924).



salt effect. We are particularly interested in the simple ionic catalysis represented by

- (1)  $A + B^+ \rightarrow AB^+ \rightarrow$  products.
- (2)  $A + B^- \rightarrow AB^- \rightarrow$  products.

The primary salt effect will be given by  $\frac{\gamma_A \gamma_{B^+}}{\gamma_{AB^+}}$  in the case of reaction (1),

and by  $\frac{\gamma_A \gamma_{B^-}}{\gamma_{AB^-}}$  in the case of reaction (2).<sup>12</sup> In dilute solutions the ratios

$\frac{\gamma_{B^+}}{\gamma_{AB^+}}$  and  $\frac{\gamma_{A^-}}{\gamma_{AB^-}}$  may be taken equal to unity, and consequently  $F$  equals  $\gamma_A$ .

The variation of  $\gamma_A$ , the activity coefficient of the neutral compound, with the ionic strength of the solution appears to be linear in solutions of moderate concentrations, and thus we obtain the primary linear salt effect.

Brönsted's expression for  $F$  is a limiting case. At higher concentrations,

$\frac{\gamma_{B^+}}{\gamma_{AB^+}}$  cannot be taken as unity nor is it likely that the simple expression

$\frac{\gamma_A \gamma_{B^+}}{\gamma_{AB^+}}$  be taken proportional to the probability that the reaction passes from

the initial to the intermediate state. Indeed, the problem seems to depend on the factors which determine the potential of the intermediate or the collision in concentrated solutions, and little hope can be entertained of obtaining a convincing theory until a satisfactory theory of concentrated solutions be developed.

Our procedure for the investigation of  $F$  has been to measure hydrogen and hydroxyl ion catalysis in acid and hydroxide solutions and in acid-salt and hydroxide-salt mixtures. We have determined the activity coefficients of acids and bases both in pure aqueous and aqueous salt solutions, and also the activity coefficients of some neutral molecules in salt solutions. We have also made an extended study of the neutral salt

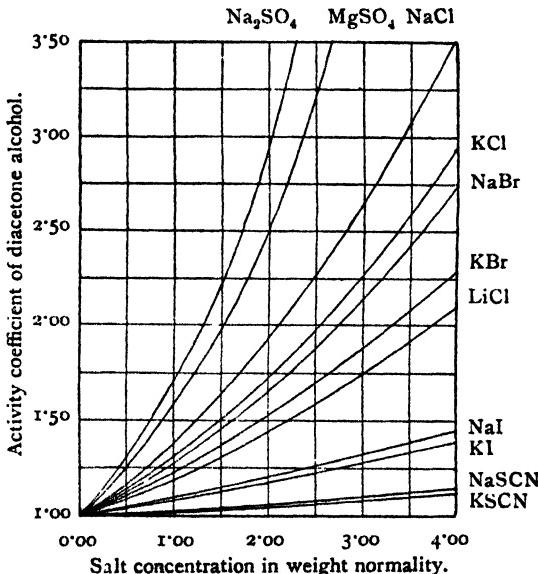


FIG. 2.—Curves for the relative activity coefficient of diacetone alcohol in various salt solutions.

<sup>12</sup> The solutions are considered to be sufficiently dilute so that  $\gamma_{B^+}$ ,  $\gamma_{B^-}$ ,  $\gamma_{AB^+}$  and  $\gamma_{AB^-}$  may be taken as square roots of ionic activity coefficient products.

catalysis of hydrogen peroxide by the iodide ion and have available the activity coefficients of the salts employed. In the discussion of the primary salt effect, we are at present only able to spread out the results of these studies and point out a few of the most important features.

### The Salt Effect on Neutral Molecules.

Recently, the activity coefficient of diacetone alcohol in salt solutions relative to unity at zero salt concentration has been determined by Åkerlöf from measurements of its partition coefficient between aqueous salt solutions and bromobenzene or cymene. The analyses were made by means of a Zeiss interferometer. The results are given in Fig. 2 in which  $\gamma_A$  is plotted against the salt concentration. For comparison, the results on the activity coefficient of ethyl acetate in salt solutions computed from the solubility measurements of Glasstone and Pound, and Glasstone,

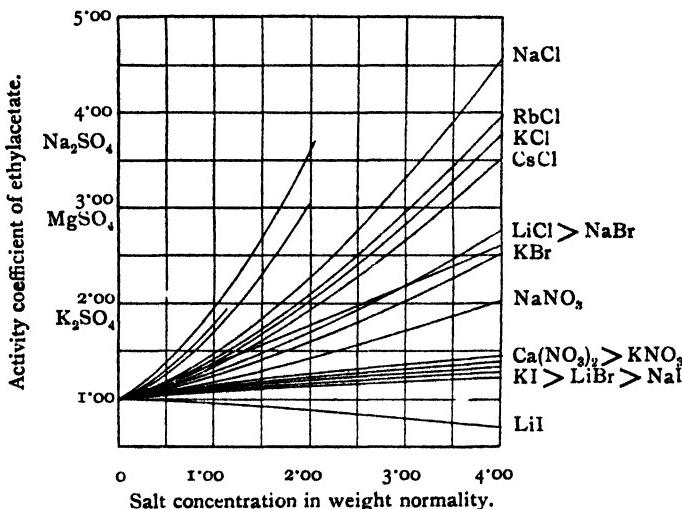


FIG. 3.—Curves for the relative activity coefficient of ethylacetate in various salt solutions.

Dimond, and Jones<sup>13</sup> are given in Fig. 3. The results are similar both in distribution and magnitude. This is important since it is evidence that both series of experimental results are reliable.

It is important to note that the distribution of these salting out coefficients does not follow the activity coefficients of the salts. The order of the results in Fig. 2 is



whereas, in the case of the activity coefficients, we find that



This fact shows that no simple relation connecting the "salting out" effects of salts and their activity coefficients is to be found.

<sup>13</sup> Glasstone and Pound, *J. Chem. Soc.*, 127, 2660 (1925); Glasstone, Dimond, and Jones, *ibid.*, 2935 (1926).

## The Neutral Salt Effect on the Acid Catalysis of Ethyl Acetate.

The graph illustrates the effect of various salt additions on the reaction velocity of ethyl acetate hydrolysis. The y-axis represents the reaction velocity multiplied by  $10^6$ , ranging from 28 to 48. The x-axis represents the salt concentration in normality, ranging from 0 to 3.00. Four straight lines are shown, all originating from the same point on the y-axis at zero concentration. The lines have different slopes, indicating different degrees of enhancement of the reaction rate by the added salt. The order of increasing salt concentration (from left to right) is: NaCl, KCl, LiCl, and NaBr.

Salt Concentration (N)	NaCl ( $k \times 10^6$ )	KCl ( $k \times 10^6$ )	LiCl ( $k \times 10^6$ )	NaBr ( $k \times 10^6$ )
0.00	28.0	28.0	28.0	28.0
1.00	35.0	33.0	31.0	30.0
2.00	42.0	39.0	37.0	36.0
3.00	48.0	45.0	43.0	42.0

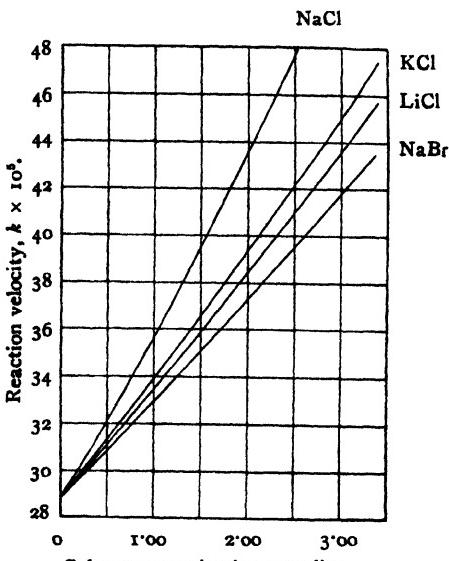


Fig. 4.—Curves for the velocity of hydrolysis of ethylacetate by 0.1 N hydrochloric acid in various salt solutions.

This is shown in Table I., Part I., where the above equation is tested at 1, 2, and 3 normal concentrations. At zero salt concentration  $k$  equals 28.8.

TABLE I.—A RELATION BETWEEN  $k \times 10^5$  AND  $\gamma$ .

### Part I—0.1*N* HCl—MX Mixtures

1N Salt.				2N Salt.				3N Salt.				
$k \times 10^5$	$\gamma_A$	$\sqrt{\gamma_A}$	$k'$	$k \times 10^5$	$\gamma_A$	$\sqrt{\gamma_A}$	$k'$	$k \times 10^5$	$\gamma_A$	$\sqrt{\gamma_A}$	$k'$	
KCl	34.1	1.46	1.21	28.2	39.4	2.02	1.42	27.7	44.6	2.75	1.66	26.9
NaCl	35.7	1.51	1.23	28.5	43.1	2.22	1.49	28.9	52.3	3.22	1.80	29.0
LiCl	33.6	1.37	1.17	28.7	38.0	1.77	1.33	28.5	42.2	2.17	1.48	28.5
NaBr	33.1	1.35	1.16	28.5	37.4	1.72	1.31	28.5	41.7	2.15	1.47	28.3

#### Part II.—0.05*N* HCl—MCl Mixtures.

KCl	15.8	1.46	1.21	13.1	17.9	2.02	1.42	12.6	20.2	2.75	1.66	12.2
NaCl	16.8	1.51	1.23	13.7	20.2	2.22	1.49	14.0	23.8	3.22	1.80	13.2

<sup>14</sup> Harned, *J. Amer. Chem. Soc.*, **40**, 1461 (1918); Bowe, *J. physical Chem.*, **31**, 290, (1927).

$\gamma_A$ , and  $\sqrt{\gamma_A}$  equal unity, and therefore  $k'$  equals 28.8. The values of  $k'$  are all in the neighbourhood of 28.5, with the exception of the 2 and 3 normal potassium chloride results. As a further test we include in Part II of the table a similar calculation on the results of Åkerlöf<sup>16</sup> on the hydrolysis of ethyl acetate by 0.05*N* hydrochloric acid in potassium and sodium chloride solutions. In this case, the value of  $k'$  is 13.8 at zero salt concentration. The result obtained is about the same as with the first series but is not quite so consistent. All the above rather scanty and not very accurate data should be redetermined with a view of obtaining more accurately the correct relation between the above quantities.

### Primary Salt Effect on the Iodide Ion Catalysis of Hydrogen Peroxide.

Fig. 5 contains the results of Harned and French<sup>16</sup> on the neutral salt catalysis of the reaction



in neutral aqueous solution. The catalyst was 0.02*N* potassium iodide and the salt concentrations are expressed in normalities.

This is a very interesting series of results, since with minor exceptions the individual salt effects are in the same order as the activity coefficients of the salts. Furthermore, the distribution of the results is quite different from that of ester hydrolysis. From the fact that the magnitude of the salt effect was the same at different catalyst concentrations, Harned concluded that the neutral salt effect was a function of the activity coefficients of the added salts rather than that of the catalyst.

Recently, Harned and Åkerlöf and Harned and Douglas<sup>17</sup> have calculated the activity coefficients of these salts by Hückel's<sup>18</sup> equation,

$$\log f = - \frac{u \sqrt{\sum c_i z_i^2}}{1 + A \sqrt{\sum c_i z_i^2}} + B \sum c_i z_i^2, \dots \quad (11)$$

<sup>15</sup> Åkerlöf, *Z. physik. Chem.*, **98**, 260 (1921).

<sup>16</sup> Harned, *J. Amer. Chem. Soc.*, **40**, 1461 (1918); French, *J. physical Chem.*, **32**, 401 (1928).

<sup>17</sup> Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926); Harned and Douglas, *J. Amer. Chem. Soc.*, **48**, 3005 (1926).

<sup>18</sup> Hückel, *Physik. Z.*, **26**, 93 (1925).

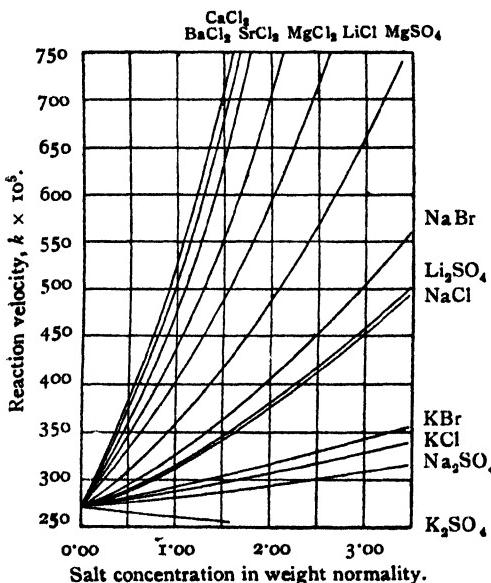


FIG. 5.—Curves for the decomposition velocity of hydrogen peroxide by 0.02*N* potassium iodide in various salt solutions.

where  $f$  is the mean activity of the electrolyte divided by its mol fraction,  $c$ , the concentration in mols per 1000 c.c. of solvent, and  $z_i$  the valence of the  $i^{th}$  ion. The first member on the right is obtained from the theory of Debye and Hückel. A is a constant characteristic of each salt, but from our calculations has nearly the same value for a salt of a given valence type.  $a$  is a universal constant. B is a constant characteristic of each salt and accounts for the difference in magnitude of the activity coefficients of the various salts. Since the plots are given in normalities and not ionic strengths, it is necessary to compare B of a univalent with 6B of a bivalent electrolyte. These values are given in Table II.

TABLE II.

## B CONSTANTS.

	B.		6B.	6B.
KCl	0.017	BaCl <sub>2</sub>	0.171	K <sub>2</sub> SO <sub>4</sub> - 0.084
KBr	0.022	SrCl <sub>2</sub>	0.180	Na <sub>2</sub> SO <sub>4</sub> - 0.030
NaCl	0.028	CaCl <sub>2</sub>	(0.360)*	Li <sub>2</sub> SO <sub>4</sub> 0.052
NaBr	0.040	* Questionable owing to inaccuracy of experimental results from which it was obtained.		
LiCl	0.070			

The general distribution of the kinetic results is the same as the B and the 6B values. The univalent salts are the best. Potassium sulphate which has a negative B-value decreases the velocity, sodium sulphate increases the velocity somewhat but has a small negative B-value. The B-values for both sodium and lithium sulphate are observed to be somewhat too low to conform with the kinetic results. Barium and strontium chlorides nearly conform, but calcium chloride is anomalous. In connection with this reaction, the determination of  $\gamma_A$ , the activity coefficient of hydrogen peroxide in the salt solutions, is a matter of considerable interest.

## The Hydroxide Ion Catalysis of Decomposition of Diacetone Alcohol.

Previous to the recent work of Åkerlöf<sup>19</sup> on the decomposition of diacetone alcohol, few accurate data were available on hydroxide ion catalysis either in aqueous or in aqueous salt solutions. The first definite relation between the velocity constants and activity coefficients was obtained in the cases of the concentrated aqueous solutions of potassium, sodium, and lithium hydroxides. This is shown by Fig. 6. In the lower part of the figure,  $\frac{k}{N}$  is plotted against  $N$ , where  $k$  is the velocity constant and  $N$  the normal concentration of the hydroxide. The distribution and form of these curves is obviously similar to those of the activity coefficients which are given in the upper part of the figure. Åkerlöf found that in the cases of sodium and potassium hydroxides at concentrations between 0.4*N* and 6*N* the equation,

$$\frac{k}{N\gamma_{MOH}} = k', \dots \quad . \quad . \quad . \quad . \quad . \quad (12)$$

<sup>19</sup> Åkerlöf, *J. Amer. Chem. Soc.*, **48**, 3046 (1926); **49**, 2955 (1927); **50**, 733 (1928); **50**, 1272 (1928).

was valid to within  $\pm 1.5$  per cent. Lithium hydroxide did not give as

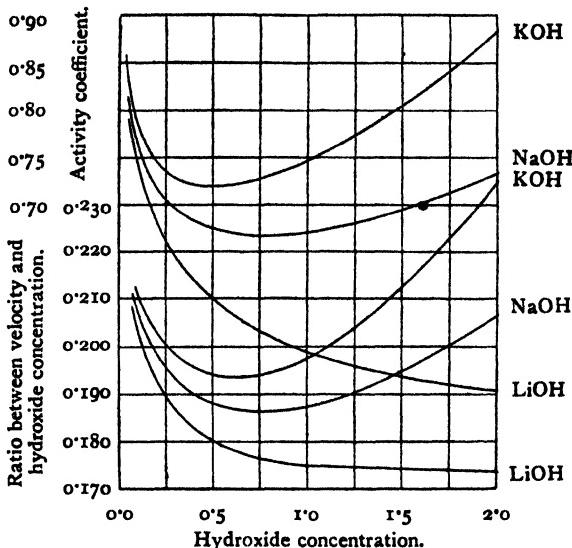


FIG. 6.—Curves for the activity coefficients of the alkali hydroxides in aqueous solutions (upper three curves), and the ratio between decomposition velocity of diacetone alcohol and alkali hydroxide concentration (lower three curves) in the same solutions.

velocity will be proportional to its concentration. We have, according to Brönsted's theory, the equation,

$$v = k' c_A c_{\text{OH}} \frac{\gamma_A \gamma_{\text{OH}}}{\gamma_i}$$

which in very dilute solutions will reduce to the simple law

$$v = k' c_A c_{\text{OH}}$$

since  $\frac{\gamma_A \gamma_{\text{OH}}}{\gamma_i}$  will equal unity. This may very well be the true relation in the very dilute solutions. In the concentrated solutions, however, we find that

$$v = k' c_A c_{\text{OH}} \sqrt{\gamma_M \gamma_{\text{OH}}} \quad . . . . \quad (12a)$$

Although  $\gamma_A$ , the activity coefficient of the diacetone alcohol, has not been determined, we find that it must have values comparable with those of the chlorides (Fig. 2), since diacetone alcohol is salted out to a considerable extent by these hydroxides. But  $\gamma_A$  does not seem to occur in the equation for the velocity constants, either in the dilute or concentrated solutions. On the basis of Brönsted's theory, this condition might be fulfilled if the intermediate was neutral, or if the effective collision required the primary effect of the hydroxyl ion and the secondary effect of the metal ion.

The whole situation becomes even less definite when we consider the neutral salt effect although it appears that the order of the kinetic salt effects is the same as that of the activity coefficients of the hydroxides in the corresponding salt solutions. This is clear from the plots in Fig. 7. The

accurate a result, but this may be due to the uncertainty in the determination of the activity coefficient. Care should be exercised in using this relation since we find that it is not valid in the hydroxide concentration range from  $0.2N$  to  $0.01N$  or less. Indeed, in these dilute solutions, the velocity constant appears to become proportional to the concentration of the hydroxide.

It is difficult to understand all this. Since the hydroxide ion is necessary for this catalysis, the

velocity constant-alkali halide concentration plots are in the lower part of the figure and the activity coefficient-salt concentration plots are in the upper part. The hydroxide concentration was  $0.1N$ . The distribution of the two sets of curves is the same. However, the relation given by equation (12) is no longer valid. In fact, when the velocity constants are divided by the activity coefficients, a quantity is obtained which first increases somewhat, then at  $0.3N$  concentration of salt passes through a maximum and finally decreases linearly with increasing salt concentration. This may be some function of the reciprocal of an ionic activity coefficient.<sup>20</sup> To further complicate

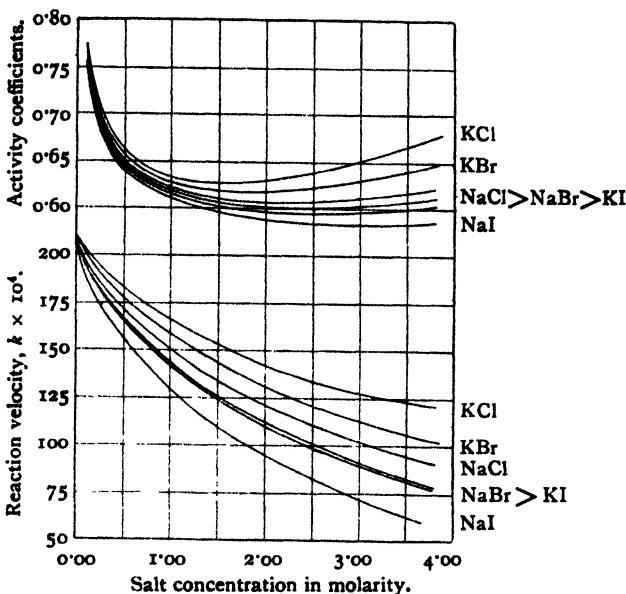


FIG. 7.—Curves for the activity coefficients of the  $0.1N$  alkali hydroxides in various salt solutions (upper curves), and the decomposition velocity of diacetone alcohol by  $0.1N$  alkali hydroxides in the same salt solutions. The abscissa of the upper curves is the total concentration.

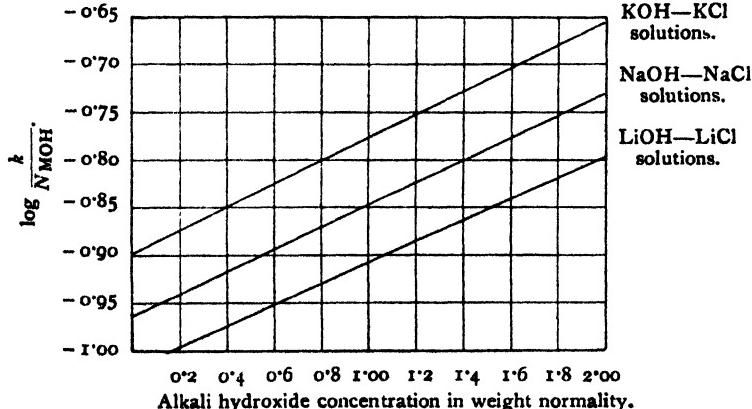


FIG. 8.—Curves for the logarithm of the ratio between decomposition velocity of diacetone alcohol and alkali hydroxide concentration in alkali hydroxide-chloride solutions at the total molarity of 2.

matters, we should point out that the distribution of the results of the salt

<sup>20</sup> Terry, *J. Amer. Chem. Soc.*, **50**, 1239 (1928).

effect on the hydroxyl ion catalysis of nitrosotriacetoneamine is somewhat different from that of the diacetone alcohol.<sup>21</sup>

In Fig. 8 we include plots of the values of  $\log \frac{k}{N_{\text{MOH}}}$  at  $2N$  total concentrations of hydroxide-corresponding chloride solutions against  $N_{\text{MOH}}$ , the normality of the hydroxide in question. The plots are straight lines and are nearly parallel. Although these plots are similar in form to similar activity coefficient plots, we have been unable to explain their nature, or to find any convincing relation between them and the thermodynamic data.

### Summary.

(1) We have emphasised the futility of attempting to solve the problems of homogeneous catalysis by the use of individual ion activity coefficients.

(2) We have shown that in cases where the catalyst is a weak electrolyte with a known dissociation constant the primary and secondary salt effects may be conveniently separated.

(3) In our studies of the primary neutral salt effect in more than six reactions, we have found no uniformity which will yield a simple and general law or rule. The distribution of the effects of the salts is quite different in each reaction. The addition of salt in acid catalysis usually tends to increase the reaction velocity, while in hydroxide catalysis the reverse is usually true, but this is not always the case. However, when we know the activity coefficients of the neutral compounds and the activity coefficient products of the catalysts, some important relations are almost certain to develop. A few such relations have been determined.

<sup>21</sup> Clibbens and Francis, *J. Chem. Soc.*, 101, 2358 (1912); Francis and Geake, *ibid.*, 103, 1722 (1913); Francis, Geake, and Roche, *ibid.*, 107, 1651 (1915); French, *loc. cit.*, n. 16.

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## KETO-ENOL ISOMERISM AND THE MECHANISM OF HOMOGENEOUS REACTIONS.

By F. O. RICE and J. J. SULLIVAN.

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During the past few years there has been a considerable extension of our knowledge of the kinetics of homogeneous reactions, especially those occurring in the gaseous phase. It seems likely that experimental studies will contribute largely to the advance of our knowledge of the mechanism of such reactions, because the difficulties of theoretical treatment especially of condensed systems are very great. The extension of experimental studies to new types of reactions or to reactions over wider ranges than previously done is therefore urgently required.

The rate of keto-enol change seemed to present a new field for such study; the change is a simple one that can easily be measured; by substitution the velocity constants can be varied over a great many orders; the

rate of the reaction can be followed in the pure liquid condition, in different solvents, and in the vapour state. Furthermore, there are at present practically no quantitative measurements available.

The present paper contains an account of some quantitative work on the rate of change of the isomeric forms of acetoacetic ester, and also some considerations on the mechanism of chemical reaction rate.

### Keto-Enol Change.

Consider the reaction  $R \cdot C(OH) : CHR \rightarrow RCOCH_2R'$ ; by making appropriate substitutions for the radicals  $R$  and  $R'$  we obtain a series of compounds which all undergo this type of change, but differ widely in velocity. Thus we have benzoyl ethyl acetate, acetyl ethyl acetate, acetyl acetone, malonic ester and acetone; these are given in increasing order of the rates of change, so far as we can judge from the semi-quantitative data available. In a carefully purified condition benzoyl ethyl acetate takes months to attain equilibrium, whereas malonic ester takes only a few seconds. The rates of these reactions are greatly affected by a variety of catalysts. Alkalies of all kinds act with great vigour; acids also catalyse the reactions, especially in non-polar solvents. Statements occur throughout the literature that traces of substances such as oxalic acid or phthalic anhydride stabilise these compounds against aminic impurities. Since the statements in literature are often contradictory, and of a qualitative character, we determined to make a quantitative study of one of these compounds. We selected acetoacetic ester since it is of considerable importance, and has been carefully investigated by Kurt Meyer and his co-workers.<sup>1</sup>

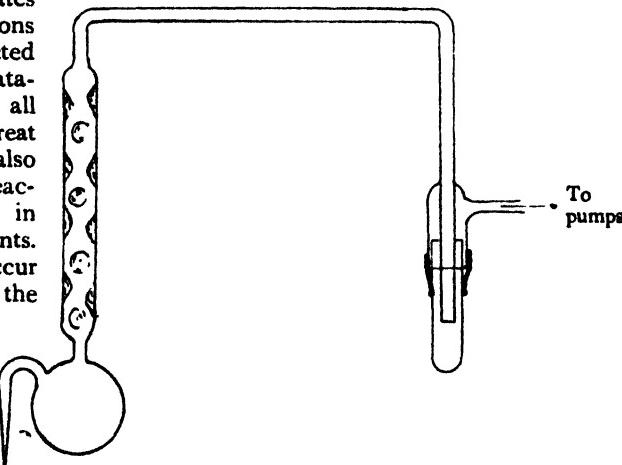


FIG. I.

In Fig. I we give a sketch showing the apparatus used to prepare the enolic form of the ester. The apparatus consists of pyrex glass, and during distillation of the ester, a high vacuum of about  $10^{-5}$  mm. is maintained by a mercury vapour pump backed by an oil pump. The receiver consists of a pyrex test tube kept at  $-80^\circ C.$  and attached to the apparatus by a ring of rubber tubing. The distillations could therefore be performed at room temperature or slightly higher so that there was a minimum of decomposition of the ester. The equilibrium form of the ester contains 7.8 per cent. enol, but the enolic form is more volatile and the distillate is about 40 per cent. enolised. Since catalytic impurities are concentrated in the distillation flask, its contents keep approximately at the equilibrium concentration,

<sup>1</sup> See *Ber.*, 1911-1923.

and thus provide a constant supply of the enolic form. A number of fractions can therefore be collected in test tubes, transferred to a thermostat, and rate measurements made. For calculation of the rate of reaction<sup>2</sup> we used the equation

$$K = \frac{2.12}{t} \log \frac{x_0 - 0.078}{x - 0.078},$$

where  $x_0$  is the initial mole fraction of enol and  $x$  is the mole fraction of enol after  $t$  hours. This equation gives very satisfactory constants, the following being a typical example of the change of acetoacetic ester at 25° C., in a pyrex glass tube:—

Hours % enol	0 36·4	43 30·1	47·3 30·4	71·5 28·6	74·5 27·6	142·5 23·6	185 20·3	236 17·7	286 15·8	330 14·2
K	—	·0053	·0046	·0041	·0045	·0038	·0041	·0041	·0041	·0042

The stability of the ester, as measured by the value of  $K$ , was very sensitive to slight traces of impurities, and the different fractions obtained by distillation from one sample varied over a wide range; this is illustrated in Table I. The term half life means the calculated time in hours which would be taken for the pure enol form to fall to 50 per cent. enol and 50 per cent. keto.

TABLE I.—STABILITY OF THE FRACTIONS OF ACETOACETIC ESTER (DISTILLED AT ROOM TEMPERATURE).

Fraction.	Initial per cent. Enol.	K.	Half Life.	Hours Observed.
1	—	—	—	—
2	30·7	0·027	29	210
3	36·9	0·016	48	300
4	31·0	0·013	58	240
5	25·2	0·0063	124	115
6	32·8	0·0047	163	260
7	35·6	0·0068	115	140
8	38·4	0·0056	128	141

We did a considerable number of experiments, attempting to obtain samples of ester of such high degree of purity that the rate of change would be negligibly small. We decided however to abandon these experiments in favour of comparative measurements on the rate of change of the ester with and without the addition of known concentrations of various substances. We found to our surprise that the addition of small quantities of substances such as acetyl chloride, carbonyl chloride, and phthalic anhydride which were recommended as stabilisers for this type of reaction were actually accelerators. We expected that the first two substances would combine with aminic impurities to give neutral carbamides and therefore have a stabilising effect similar to that found by Lowry and Magson<sup>3</sup> in the case of nitrocamphor. A possible explanation of this may perhaps be found in the presence of slight traces of water in the acetoacetic ester. We dried the ester in the final stage with anhydrous copper sulphate; the vapour

<sup>2</sup> See Rice and Sullivan, *J. Amer. Chem. Soc.*, 48 (1928).  
<sup>3</sup> *J. Chem. Soc.*, 93, 107 (1908); *ibid.*, 83, 1316 (1903).

pressure<sup>4</sup> of the system  $\text{CuSO}_4 - \text{CuSO}_4 \cdot \text{H}_2\text{O}$  is 0.8 mm. at 25°C., and assuming this concentration present in the ester we have one part of water per 1,000,000 parts of ester approximately. Several catalysts, such as piperidine or ammonia, even when present in concentration of  $N/10,000,000$ , greatly affect the rate of change, so that the problem of removing these traces is a very difficult one.

In Table II. we give the effect of alkaline catalysts and bromine on the rate of change of the ester. The second column gives the ratio of the rates of change of the ester before ( $K_1$ ) and after ( $K_2$ ) the addition of the catalyst.

TABLE II.—EFFECT OF ALKALINE CATALYSTS IN ACETOACETIC ESTER.

Catalyst.	$K_2/K_1$ .
Piperidine	11,400
Ammonia	4,000
Pyridine	264
Quinoline	17
Bromine	1,300

The concentration of catalyst in each case was  $4 \times 10^{-5} M$ .

We are unable to explain the high value for bromine; it cannot be due to the formation of hydrobromic acid because this does not catalyse the reaction nearly so strongly as the alkalis. It may be noted that Rumeau<sup>5</sup> found that bromine is a powerful catalyst, whereas iodine has no such effect.

The results obtained so far in this work are only preliminary and the work is now being extended to other catalysts and other keto-enol tautomers.

### The Mechanism of Chemical Reaction Rate.

Before discussing this subject it seems desirable to bring together certain experimental work which appears to have some significance in this connection. Recently Francis<sup>6</sup> has measured the rate of bromination of a large number of aromatic, phenolic and aminic derivatives. Most of these reactions are very rapid and the absolute values of the velocity constants are not very accurate; however, relative values at different temperatures were carefully measured and the results showed that although the velocities varied over a very wide range the temperature coefficients were the same within experimental error. Conant and co-workers<sup>7</sup> have investigated the reaction between organic chlorides and potassium iodide in which a simple metathesis occurs, to give the organic iodide and potassium chloride. The velocities varied over a million-fold, but here also the temperature coefficients are the same within experimental error. Several other examples of this sort could be quoted, and this behaviour led one of us<sup>8</sup> to adopt the unhydrated hydrogen ion hypothesis; this hypothesis, however, is not supported by results obtained in alkaline solution<sup>9</sup> nor by results in buffer solutions.<sup>10</sup> At present it seems probable that such changes as keto-enol tautomerism, or other changes involving complicated molecules, cannot be satisfactorily explained by such a collision hypothesis. The mechanism which appears most promising to us is a unimolecular one developed on

<sup>4</sup> Foote and Scholes, *J. Amer. Chem. Soc.*, **33**, 1309 (1911).

<sup>5</sup> Rumeau, *Bull. Soc. chim.*, **35**, 762 (1924).

<sup>6</sup> Francis, *J. Amer. Chem. Soc.*, **48**, 655 (1926).

<sup>7</sup> Conant and Kirner, *J. Amer. Chem. Soc.*, **46**, 232 (1924).

<sup>8</sup> Rice, Frying and Wesolowski, *J. Amer. Chem. Soc.*, **46**, 2405 (1924).

<sup>9</sup> Schmid and Olsen, *Z. physikal. Chem.*, **124**, 97 (1926); Kilpatrick, *J. Amer. Chem. Soc.*, **48**, 2091 (1926); Åkerblöf, *ibid.*, **48**, 3046 (1926).

<sup>10</sup> Bolin, *Z. anorg. Chem.*, **142**, 201 (1925).

a basis of statistical mechanics rather than thermodynamics. Two unimolecular reactions, the decomposition of nitrogen pentoxide<sup>11</sup> and the racemisation of pinene<sup>12</sup> have been measured over great ranges of concentration. The racemisation of pinene gave practically the same constant when measured in the gaseous and liquid state, and in solution in petroleum, acetophenone and  $\alpha$ -methyl napthalene. Similarly the decomposition of nitrogen pentoxide gave the same value whether in the gaseous state or in organic solvents;<sup>13</sup> the rate of decomposition in the solid state has not yet been measured. When dissolved in 100 per cent. nitric acid, nitrogen pentoxide decomposes at one tenth of the normal rate, this being the only example we have in which the rate of decomposition of nitrogen pentoxide has been affected without changing the temperature. It seems significant that in this experiment we might expect the nitrogen pentoxide to form an addition compound with the nitric acid to some extent.

These results appear to us to be of considerable significance in connection with such experiments as those described in this paper, and appear to indicate that the internal energy of a molecule at any given temperature is very characteristic and is independent of the state of the substance.<sup>14</sup> The energy of a molecule is composed of translational energy, rotational energy, and the internal energy associated with the vibrational degrees of freedom of the parts of the molecule. There is some evidence that at collision, translational energy is not readily transferred to internal energy and *vice versa*. For example, the absorption of sound waves in gases has hitherto been explained by internal friction and heat conduction. If, however, there is a slow rate of exchange between the translational movement and the internal degrees of freedom of the molecules, this will also increase the absorption; the experimental data available show that this new effect is either of considerable influence or even predominant.<sup>15</sup>

The main difficulty we meet when we limit ourselves to the internal degrees of freedom of the molecules is in connection with the rate of activation, since Fowler and Rideal<sup>16</sup> showed that it was necessary to make the somewhat extreme assumption that on collision between two molecules the whole of the internal energy and the relative kinetic energy flowed into one molecule; similar calculations, but without this assumption, have been made, using quantum mechanics instead of classical mechanics, and the results give rates of activation much greater than the measured rates of decomposition even of nitrogen pentoxide at low pressures. It would appear, therefore, that the theoretical objections to activation by collision disappear.

We suggest, therefore, a unimolecular mechanism for the change enol form  $\rightarrow$  keto form; the enolic form or a complex with a catalyst undergoes a change dependent on the concentration, and quite independent of the time between collisions; the rate is determined by a process occurring inside the molecule or the complex and this in turn is determined by the number of internal degrees of freedom. The work has not yet progressed far enough to put this to the experimental test in the case of keto-enol changes.

<sup>11</sup> Daniels and Johnson, *J. Amer. Chem. Soc.*, **43**, 27 (1921); for a summary of the work see Rice and Getz, *J. Physical Chem.*, **31**, 1572 (1927).

<sup>12</sup> Smith, *J. Amer. Chem. Soc.*, **49**, 43 (1927).

<sup>13</sup> Lueck, *J. Amer. Chem. Soc.*, **44**, 757 (1922); Rice and Getz, *J. physical Chem.*, **31**, 1572 (1927).

<sup>14</sup> For a complete presentation of this and the following matter see Urey and Rice, *J. Amer. Chem. Soc.*, **50** (1928).

<sup>15</sup> Herzfeld and Rice, *Physical Rev.*, **31**, 691 (1928).

<sup>16</sup> Fowler and Rideal, *Proc. Roy. Soc., A*, **113**, 570 (1927).

# DETERMINATION OF THE CATALYTIC COEFFICIENT OF THE HYDROXYL ION IN THE MUTAROTATION OF GLUCOSE AND LACTOSE.

By THOMAS MARTIN LOWRY AND GORDON LESLIE WILSON.

*Received 9th October, 1928.*

When determining the catalytic coefficients of the various molecules and ions which promote the mutarotation of glucose, no difficulty is experienced in deducing a trustworthy value for the hydrogen (or oxonium) ion, since the concentrations of hydrochloric acid which are required to produce a suitable acceleration are of a convenient order of magnitude, and conditions are easily obtained in which the acceleration produced by these ions is far greater than that produced by the other catalytically-active components of the solution. The coefficient for the undissociated molecules of a weak acid can also be determined without difficulty, and with a reasonable degree of accuracy, by making a suitable allowance for the oxonium ions with the help of measurements of electrode potential. In the case of a strong acid, however, the concentration of the undissociated molecules only becomes important when the mutarotation is too fast for convenient observation; moreover, no trustworthy method is yet available for determining the "coefficient of ionisation" of the acid at these concentrations, since the formulæ of Arrhenius and of Debye and Hückel are equally inapplicable to concentrated solutions of a strong electrolyte of the type of hydrogen chloride, which is capable of forming covalent molecules in solution, as well as in the homogeneous solid, liquid, or gaseous state. The coefficients deduced for the molecules of HCl can therefore only be regarded as rough approximations, although the qualitative conclusion that they are more efficient than the oxonium ions of the dissociated acid is of great interest and importance.

The determination of the catalytic coefficient of the hydroxyl ion also presents peculiar difficulties, mainly on account of its extraordinary magnitude. Thus, whereas an appreciable acceleration is only produced by *acids* at a concentration of about  $N/100$ , in the case of an *alkali* a similar acceleration is produced at a concentration of  $N/1,000,000$ . Thence follows the dilemma, on the one hand, that the catalytic activity of "buffer solutions" of such small alkalinity is determined to a far larger extent by the catalytically active salts than by the minute proportion of hydroxyl ions which they contain, and, on the other hand, that, if a free alkali is used, the catalytic activity will probably be that of a bicarbonate and not of a hydroxyl ion,  $\text{OH}' + \text{CO}_2 \rightleftharpoons \text{HO} \cdot \text{CO} \cdot \text{O}'$ . On account of these peculiar difficulties it is scarcely surprising that, in the paper in which the widespread catalytic activity of acid and basic ions and molecules in mutarotation was first established,<sup>1</sup> the alkaline arm of the catalytic catenary diverged widely from that plotted by Euler and by Kuhn and Jacob, although the acid arm of the catenary agreed very well with that plotted by these authors. The conclusions drawn from these observations were therefore limited to a statement "that the catalytic coefficient of the hydroxyl ion is probably less than

<sup>1</sup> Lowry and Smith, *J. Chem. Soc.*, 1927, 2539; compare Brönsted and Guggenheim, *J. Amer. Chem. Soc.*, 49, 2554 (1927).

$k_e = 20,000$ , since this number includes the catalytic activity of the bicarbonate ions, as well as of the hydroxyl ion." The present paper describes a series of experiments which were carried out in order to determine the true value of this coefficient in the mutarotation of glucose and of lactose in aqueous solutions at 20°.

For this purpose, experiments were first made with buffer solutions, in order to find out whether a trustworthy value for the hydroxyl ion could be obtained by using solutions containing diminishing concentrations of the saline components and finally extrapolating to zero concentration. A solution containing  $N/20$  boric acid and  $N/5$  sodium borate was selected, giving  $\rho_H = 8.84$ , as measured with a hydrogen electrode. This  $N/20$  solution of boric acid was then diluted to  $N/40$  and  $N/100$ , and slight adjustments in the proportions of boric acid and sodium borate were made to retain the  $\rho_H$  value at 8.84. The velocity-coefficients for the mutarotation of lactose in the three buffer solutions were 0.71, 0.38 and 0.13. Since the velocity-coefficient for the hydroxyl ions at this alkalinity is only about 0.035 (see below), it appeared that the effect of the borate ions would only be reduced to equality with that of the hydroxyl ions if the concentration of the buffer solution were reduced to about  $N/300$ , and that dilution to  $N/1000$  would be necessary in order to secure (even by extrapolation) a trustworthy value for the hydroxyl ion alone. Since the solution could scarcely be expected to be an efficient buffer at these extreme dilutions, the method was abandoned in favour of measurements with alkaline solutions containing no boric acid.

The success of these experiments depended on the possibility of excluding contamination by carbon dioxide, more particularly during the stage at which the solution is being transferred from the polarimeter tube to the electrode cell in order to measure its alkalinity. Preliminary experiments were therefore made in order to see whether this transfer could be effected successfully in solutions to which no sugar had been added. For this purpose 25 c.c. of water, which had been redistilled, and freed from carbon dioxide by boiling it in a silica flask, was transferred to a graduated tube, which had been swept out with air free from carbon dioxide. A  $N/20$  solution of sodium hydroxide, free from carbonate, was put into a small burette, which could be closed by a cap over the nozzle and weighed; a few drops of alkali from this burette were added to the boiled water, giving a concentration of about  $N/1000$  NaOH. This dilute solution was transferred to a polarimeter tube (freed from carbon dioxide) and then to a hydrogen electrode surrounded by a stream of purified hydrogen. The  $\rho_H$  was measured immediately, and the ionisation-constant for water was then calculated from the concentration of the alkali and the electro-motive force of the cell. The values thus deduced are shown in Table I. and are plotted (against temperature) in Fig. 1, where the dotted line shows the accepted values of this constant at different temperatures. The concordance of the values showed that the hydroxyl ions in these alkaline solutions were still uncarbonated, and that the solution had not been contaminated substantially with carbon dioxide during the manipulation described above.

A series of determinations with sugar-solutions was carried out as follows. The sugar was placed in the graduated tube, and dissolved in water before the alkali was added. The solution was transferred to the polarimeter tube, and the electrode-potential was measured after mutarotation was complete. The concentration of the sugar was deduced from the final rotatory power of the solution, and this value was then corrected for the fraction of sugar

present as ions. The concentration of hydroxyl ions was calculated from the electrode potential by making use of the values of  $K_w$  recorded above, since these were determined under similar conditions, and errors due to

TABLE I.—BLANK EXPERIMENTS.

Temperature.	Log [OH'].	$P_H$ .	Log $K_w$ .
16·5	4·89	11·08	15·81
16·6	4·96	11·13	15·83
17·0	4·90	10·99	15·91
17·5	4·89	11·00	15·89
17·5	4·82	10·85	15·97
17·8	3·74	11·88	15·86
17·8	4·05	10·92	15·93
18·0	4·85	10·94	15·91
18·3	4·84	10·89	15·95
19·0	4·88	10·91	15·97
19·0	4·99	11·02	15·97
19·1	4·80	10·79	14·01
19·5	4·83	10·88	15·95
19·5	4·80	10·76	14·04
20·0	4·87	10·77	14·10
20·5	4·87	10·80	14·07
20·5	4·87	10·67	14·20
21·7	4·92	10·86	14·06

liquid-liquid potentials would thus be largely eliminated. The concentration of hydroxyl ions was also deduced on the assumption that the sugar

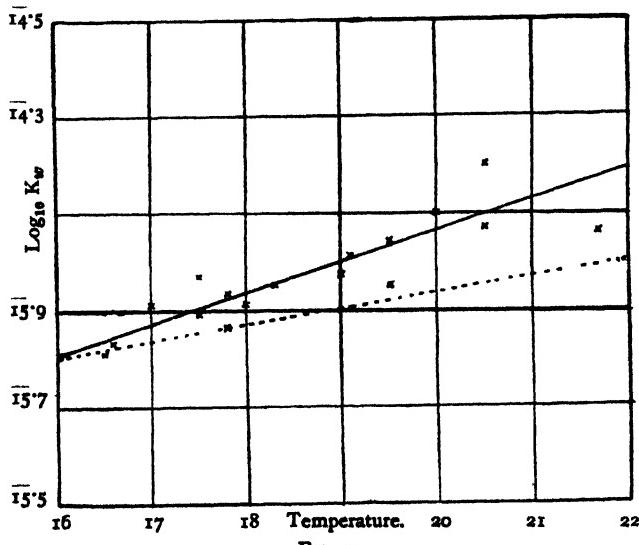


FIG. 1.

forms a salt, which is hydrolysed according to the law of mass-action, as expressed by the equation

$$\frac{[\text{OH}'] [\text{sugar}]}{[\text{sugar ion}']} = K_H.$$

Taking the acid dissociation constant for lactose<sup>2</sup> as

$$K_A = \frac{[H^+] [\text{sugar ion}']}{[\text{sugar}]} = 6.0 \times 10^{-13},$$

and remembering that  $K_A \times K_H = K_w$ , we can deduce the value of  $K_H$  by using the data for  $K_w$  in Fig. 1, and in this way we can find an independent value for  $[\text{OH}']$ . The catalytic coefficients of the hydroxyl ion, as deduced by the first method from the formula  $k_{\text{OH}} = (k_e - k_{e, \text{water}}) \frac{[H^+]}{K_w}$ , are given in the fourth column of Table II (a); those deduced by the second method, from the formula  $k_{\text{OH}} = (k_e - k_{e, \text{water}})/[\text{OH}']$ , are given in the fifth column. These calculations are subject to small errors owing to

TABLE II.—CATALYTIC-COEFFICIENTS.

Sugar.	Velocity Coefficient $k_e$ .	$\rho_H$ from E.M.F.	Value of $K_w$ .	Catalytic-Coefficient at 20°.	
				(a) $[H] (k_e - k_{e, \text{water}})$ $\frac{[H]}{K_w}$	(b) $(k_e - k_{e, \text{water}})$ $/[\text{OH}']$
(a) Lactose	0.0906	9.33 at 16.5°	$0.69 \times 10^{-14}$	5400	4100
	0.115	9.68 "	0.69 "	4700	4800
	0.194	9.69 "	0.69 "	5400	4800
	0.262	9.65 "	0.69 "	(8100)	4400
	0.493	10.08 at 16.0	0.65 "	6300	5000
Mean values =				<u>5500</u>	<u>4600</u>
(b) Glucose	0.0804	9.07 at 16.5	$0.69 \times 10^{-14}$	8100	7900
	0.115	—	—	—	7900
	0.175	9.35 at 17.8	0.84 "	8300	8500
	0.232	9.40 at 20.0	1.16 "	7600	10,100
	0.332	9.58 at 9.5	1.08 "	7600	7000
Mean values =				<u>7900</u>	<u>8300</u>
(c) Tetramethyl glucose	0.126	10.05 at 16.5°	$0.69 \times 10^{-14}$	1400	
	0.126	9.93, 14°	0.47 "	[2800]	
	0.332	10.54, 13°	0.41 "	[2200]	
	0.199	10.03, 20.5°	1.25 "	1400	
	0.133	9.86, 19°	1.01 "	1600	
	0.072	9.45, 19.5°	1.08 "	1900	
	0.343	10.25, 19.5°	1.08 "	1700	
	Mean value =				<u>1600</u>

variations of temperature, since  $k_e$  and  $k_{e, \text{water}}$  are the velocity-coefficients for the mutarotation of lactose in solutions and in water at 20°, whereas the electrode potentials used in column 4 were at 16.5°, and the dissociation-constant of Michaelis and Rona, which was used to calculate the numbers in column 5 was for a temperature of 18°.

A similar series of measurements on the mutarotation of glucose in alkaline solutions is set out in Table II (b). The catalytic coefficients in column 4 are based on measurements of electrode-potentials, using the values of  $K_w$  taken from Fig. 1. The coefficients in column 5 are based on the value of the acid dissociation constant of glucose,  $K_A = 6.6 \times 10^{-13}$

<sup>2</sup> Michaelis and Rona, *Biochem. Z.*, 1913, 49, 232.

at  $20^\circ$ , given by Kuhn and Jacob,<sup>3</sup> and the value of  $K_w$  at  $20^\circ$  was used throughout in order to calculate the value of  $K_H$  at this temperature. The agreement between the two columns is rather closer than in the case of lactose, and suggests that the acid dissociation-constant assigned to that sugar may be too low.

Data for the catalytic-coefficient of tetramethylglucose are given in Table II (c); but, since the acid dissociation-constant of the sugar has not been determined, these coefficients were deduced only from measurements of electrode potentials.

### Summary.

The final values of the catalytic coefficients are as follows:—

Lactose . . . . .	$k_{OH} = 5,000$
Glucose . . . . .	$k_{OH} = 8,000$
Tetramethylglucose . . . . .	$k_{OH} = 1,600$

The wide variation in the value of this constant, in sugars which are so closely related to one another, and which undergo mutarotation with very similar velocities in water ( $k_e = 0.0108, 0.0146, 0.0128$ ) is a noteworthy result of the present research.

One of us (G. L. W.) desires to express his thanks to Messrs. Nobel Industries, and particularly to Mr. Rintoul, for a research scholarship held during the course of this work.

<sup>3</sup> *Z. physik. Chem.*, 1924, 113, 418; Michaelis and Rona (*loc. cit.*) gave  $K_A = 6.6 \times 10^{-13}$  at  $18^\circ$ , whilst Euler, Myrbäck and Rudberg (*Arch. Kemi Min. Geol.*, 1923, 8, No. 28) gave  $K_A = 11.6 \times 10^{-13}$  at  $18^\circ$ .

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## ON THE KINETICS OF ACID AND BASIC CATALYSIS.

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There are numerous reactions which are catalytically accelerated by acids or bases or both.<sup>1</sup> If  $A \rightarrow B$  is such a reaction, we can express its kinetics in dilute aqueous solutions (*i.e.* solutions poor in electrolytes) with great accuracy by the equation for a series of simultaneous actions, as follows:<sup>2</sup>

$$\frac{d[B]}{dt} = (k_w + k_a[H'] + k_b[OH']) [A] . . . . . \quad (1)$$

where the bracketed symbols are concentrations and the  $k$  figures are velocity constants. In this equation (which shows that the reaction is accelerated by hydrogen and hydroxyl ions  $k_w$ ) is the constant of the uncatalysed reaction or "water reaction,"  $k_a$  the constant of the reaction

\* Communicated in summary at the meeting by Professor Lowry.

<sup>1</sup> J. N. Brönsted, *Om Syre- og Basekatalyse*, Kopenhagen, 1926; A. Skrabal, *Z. Elektrochem.*, 33 (1927), 322; F. O. Rice, *The Mechanism of Homogeneous Organic Reactions*, New York, 1928.

<sup>2</sup> R. Wegscheider, *Z. physik. Chem.*, 30 (1899), 593, and 41 (1902), 52.

promoted by  $H^+$  or the "acid reaction," and  $k_b$  is the constant of the "basic reaction" promoted by  $OH^-$ .

Since  $H^+$  and  $OH^-$  interact with great velocity to form water when their equilibrium is disturbed,  $[H^+]$  and  $[OH^-]$  are not independent of one another but are connected by the equation :—

$$[H^+][OH^-] = w \quad \dots \quad \dots \quad \dots \quad (2)$$

where  $w$  represents the ion product of the water. The establishment of the fact that a substance K acts as a catalyst is a matter of classification and provides no explanation of the phenomenon. The explanation or meaning of what happens is first given when the so-called "mechanism" of the reaction is revealed and firmly established; in this respect a catalytic reaction differs in no way from one which is not catalysed, although it may be remarked incidentally that many workers deny the existence of uncatalysed reactions at all.<sup>3</sup>

With the object of understanding the mechanism of the reaction of acid and basic catalysis we will consider the general reaction  $A \rightarrow B$  which, on account of its simplicity, we will take as monomolecular and irreversible. Since we are dealing with homogeneous catalysis, moreover, and suppose that the proportion of catalyst K is very small, so that it does not substantially influence the medium, and "medium catalysis" is clearly excluded, we are led to explain the phenomenon as "intermediate compound" or "chain" catalysis. We assume also that the catalyst K forms with the substrate A (or the product of its reaction) an intermediate compound Z which reacts either directly or by further formation of intermediates to give B and set free the catalyst. If  $A \rightarrow B$  is a complex reaction (*i.e.* one which proceeds by stages) the concentrations at any one time of all the intermediate compounds are small, within the range of measurability of the reaction, in comparison with A, B and K.<sup>4</sup>

We must then divide the reaction  $A \rightarrow B$  at least into the following partial reactions :—



from which the following is deduced for the velocity of the complete reaction

$$\frac{d[B]}{dt} = k[K][A] \quad \dots \quad \dots \quad \dots \quad (4)$$

Equation 3 contains the idea that every transformation which takes place between two components proceeds also in the opposite direction, a hypothesis which has been suggested by many chemists (H. E. Armstrong,<sup>5</sup> A. Kekulé,<sup>6</sup> H. Wieland,<sup>6</sup> etc.), and to which it is practically impossible to take exception.

From this it follows that the reacting substance A must have basic properties if the catalyst K is an acid, and acid properties of the catalyst is a base, for all substances which combine with acids are bases and *vice versa*.

<sup>3</sup> See A. Mittasch, *Ber.*, 59 (1926), 13.

<sup>4</sup> The range during which measurements are possible is in the middle of the reaction; for many reasons measurements cannot be taken at the beginning and end. This middle range corresponds to about 1 to 99 per cent. of the period, but as a rule the reactions are measured over a smaller range.

<sup>5</sup> See J. W. Mellor, *Chemical Statics and Dynamics*, London, 1904, and elsewhere.

<sup>6</sup> Rec. Trav. Chim. 41 (1922), 576.

Experience confirms this conclusion. Thus the typical ethers have no acid properties but are most decidedly basic (Oxonium bases); experiment shows that their hydrolysis is only catalysed by acids. The esters on the other hand are both bases and acids, which follows for example from the existence of the compounds  $\text{CH}_3\cdot\text{COOC}_2\text{H}_5\cdot\text{HBr}$ <sup>7</sup> and  $\text{C}_6\text{H}_5\cdot\text{COOC}_2\text{H}_5\cdot\text{NaOCH}_3$ .<sup>8</sup> This accords with the behaviour of the esters on hydrolysis, since this is accelerated both by acids and by bases.

It follows, further, from what has been said that the intermediate compound Z, since it is formed from an acid or a base must be of the nature of a salt or an ion. Since salt formation or neutralisation proceeds very imperfectly—the intermediate compound Z is always present in only very small concentration—the substrate A can be only a weak base or a weak acid (or pseudo-acid) or an amphotelyte. Up to this stage all workers who are concerned with the experimental or theoretical problem are of one opinion. Differences of opinion emerge when we attempt to deduce equation (4) for scheme (3).

According to the relative values of the three velocity constants  $k_1$ ,  $k_2$ ,  $k_3$  two cases can be distinguished.<sup>9</sup>

*Case (1).*—If the reversible reaction which leads to the formation of Z is sufficiently rapid compared with the further transformation of the intermediate product, the equilibrium  $A + K \rightleftharpoons Z$  is firmly established. When the equilibrium is restored the progress of the reaction in this direction is inhibited and the formation of B can go forward only as the intermediate product is eliminated by the reaction  $Z \rightarrow B + K$ . The latter part of the reaction then determines its velocity and one can write in its time equation the equilibrium values for Z, thus:—

$$\frac{d\text{B}}{dt} = k_3[Z] = k_3 \frac{k_1}{k_2} [\text{A}][\text{K}] = k_3 G[\text{A}][\text{K}] \quad . \quad . \quad . \quad (5)$$

where  $G = k_1/k_2$  represents the equilibrium constant of the reaction  $A + K \rightleftharpoons Z$ .

Combining this with equation (4) it follows that the measured velocity constant  $k$  that:—

$$k = k_3 \frac{k_1}{k_2} = k_3 G. \quad . \quad . \quad . \quad . \quad (6)$$

It will be seen that the measured velocity constant  $k$  of the complete reaction is proportional to the kinetic constant  $k_3$  as well as to an equilibrium constant G. We can call such kinetic quantities "complex-kinetic" constants.<sup>10</sup> Arrhenius<sup>11</sup> was the first who, in order to explain the large temperature coefficient of  $k$ , had recourse to velocity constants of the form (6). We will therefore call our unstable intermediate Z an "*Arrhenius intermediate*."

Equation (6) represents mathematically Euler's hypothesis of acid and basic catalysis, and the Arrhenius intermediate Z is, according to Euler, the reactive ion. I have recently shown<sup>12</sup> that this hypothesis has not yet been proved; in order to prove it one must experimentally ascertain, in addition to  $k$ , both G and  $k_3$  and show that  $k = k_3 G$ . It is the more

<sup>7</sup> O. Maass and D. McIntosh, *J. Amer. Chem. Soc.*, **34** (1922), 1273.

<sup>8</sup> H. von Pechmann, *Ber.*, **31** (1898), 501.

<sup>9</sup> See A. Skrabal, *Annalen Physik*, [4], **84** (1927), 624.

<sup>10</sup> A. Skrabal, *Monatsh. Chem.*, **37** (1916), 495.<sup>r</sup> <sup>11</sup> *Z. physik. Chem.*, **4** (1889), 226.

<sup>12</sup> A. Skrabal, *Z. Elektrochem.*, **33** (1927), 322. See also T. M. Lowry, *J. Chem. Soc.*, 1927, 2554.

difficult to bring about this proof inasmuch as both  $G$  and  $k_3$  are either only just within or entirely outside the limits of measurement. In order to measure both these values one must moreover use strongly acid or strongly basic solutions and therefore work under quite different conditions of concentration than when ascertaining the value of  $k$ . One must reduce the three values to the same concentration by a procedure of which we have no real knowledge. The more recent papers of the Euler school have not, in fact, appreciably affected this point.

*Case (2).*—The second case is given if the constant  $k_3$  in the reaction  $Z \rightarrow B + K$  is sufficiently large. In that case the formation of  $Z$  governs the velocity and the corresponding differential equation reads:—

$$\frac{d[B]}{dt} = k_1[A][K] \quad \dots \quad \dots \quad \dots \quad \dots \quad (7)$$

or if we combine this with equation (4):—

$$k = k_1 \quad \dots \quad \dots \quad \dots \quad \dots \quad (8)$$

This equation also expresses the velocity of formation of the intermediate body  $Z$ . We will call the unstable intermediate body with this characteristic behaviour the "*van't Hoff intermediate*," since J. H. van't Hoff has assumed such intermediate products in order to explain many reactions of a lower order than might be expected from their chemical equations.<sup>14</sup>

The van't Hoff intermediate, so far as concerns the part it plays in the stage-by-stage reaction, does not differ in form from the "critical complex" of R. Marcellin<sup>15</sup> and J. N. Brönsted.<sup>16</sup> On the other hand it is considered that compared with the Arrhenius intermediate it is by far more unstable, although intermediate stages between the two intermediates may exist, since by integration of the system (3) the constant  $k$  of equation (4) for an unstable  $Z$  assumes the general form:

$$k = \frac{k_1}{k_2 + k_3} \quad \dots \quad \dots \quad \dots \quad \dots \quad (9)$$

which according to the relative values of  $k_2$  and  $k_3$  becomes either equation (6) or (8).

Erich Müller<sup>17</sup> gave an explanation of acid and basic catalysis which arose from a kinetic consideration of equation (8), *i.e.*, from the assumption of a van't Hoff intermediate  $Z$ . Starting from the conception of the electron constituted molecule, he showed that on saponifying an ester with water alone four of the atoms taking place in the reaction must come together in the molecule at the same moment, whereas on the other hand if the saponification were effected by hydroxyl ions or by hydrated hydrogen ion two atoms sufficed. In this case the first stage of the reaction is decisive for its progress, so that the theory of equation (8) serves for Müller's explanation of the phenomena.

The correctness of this theory is still more difficult of kinetic proof than

<sup>14</sup> H. von Euler and A. Oelander, *Z. Elektrochem.*, 33 (1927), 527; A. Oelander, *Z. physik. Chem.*, 129 (1927), 1; H. von Euler and A. Oelander, *Z. physik. Chem.*, 131 (1928), 107.

<sup>15</sup> See for example J. H. van't Hoff and E. Cohen, *Chemische Dynamik*, Amsterdam and Leipzig, 1896, Seite 104.

<sup>16</sup> *Ann. Physique*, [9], 3 (1915), 120.

<sup>17</sup> *Z. physik. Chem.*, 102 (1922), 169; 115 (1925), 337.

<sup>17</sup> *Ibid.*, 134 (1928), 190. See also *Z. Elektrochem.*, 31 (1925), 46; 33 (1927), 253 and 561.

that of equation (6), on account of the instability of the van't Hoff intermediate. It can only be proved indirectly, namely by showing that the relation (6) is not correct.

The difficulty, inherent when seeking an explanation of chemical facts by kinetic measurements, lies in the many ways in which the velocity equation can be interpreted, as H. Goldschmidt<sup>18</sup> and especially R. Wegscheider<sup>19</sup> have repeatedly pointed out. Kinetic measurement of the velocity of the reaction  $A \rightarrow B$  furnishes only the constant  $k$  of the total reaction. In order to ascertain the mechanism of the reaction it is necessary to ascertain in equation (9) the constants  $k_1$ ,  $k_2$  and  $k_3$  of the separate intermediate reactions; the possibility of doing this is so much the more improbable as the intermediate products are the more unstable. On the other hand, it is just this great instability which is the reason why the process  $A \rightarrow B$  goes not directly but through intermediate products.<sup>20</sup>

The kinetic studies of T. M. Lowry<sup>21</sup> gave a really clear conception based upon experimental observations; they consisted in the study in non-aqueous media of the reactions to which in aqueous media the time relationship (1) applies. The experiments in these media make it practically essential to modify the old ideas as to acid and base which resulted from the studies in aqueous solution of S. Arrhenius and W. Ostwald. According to the definition given by J. N. Brönsted<sup>22</sup> and T. M. Lowry,<sup>23</sup> acids are bodies which give up a proton and bases are bodies which accept a proton. Between both kinds of bodies the following chemical equilibrium exists—



which can be known as the Acid-Base equilibrium.

In order to avoid confusion with the old narrow views, which can be retained and will be retained, for aqueous solutions, the newly-defined view formulated in equation (10) suggests the new names "*proton-donor*" for acids and "*proton-acceptor*" for bases. Amphotytes are both proton-donor and proton-acceptors, although the later view is really wider.<sup>24</sup>

The phenomenon we have been considering is then proton-donor and proton-acceptor catalysis, and kinetic equation (1) must be generalised and perfected, by introducing a separate figure for each proton-donor and proton-acceptor (J. N. Brönsted,<sup>25</sup> H. M. Dawson<sup>26</sup>). The hydroxyl-ion is a proton-acceptor; the hydrogen-ion itself is not a proton but a proton-donor, i.e., a hydrated (solvated) proton or oxonium-ion in which the hydrogen nucleus has attached itself to a molecule of water and has thus acquired the electron shell of the inert gas helium.<sup>27</sup>

For the study of the medium effect there are several particularly suitable reactions which in water proceed with considerable velocity even when uncatalysed, i.e., in which  $k_w$  of equation (1) is relatively large. Amongst these is the mutarotation of the sugars. For instance the mutarotation of glucose is uninfluenced by acidity throughout the wide range of 6.5 units

<sup>18</sup> Z. Elektrochem., 11 (1905), 5; 14 (1908), 583.

<sup>19</sup> Z. physik. Chem., 36 (1901), 543; Z. Elektrochem., 14 (1908), 133.

<sup>20</sup> See J. N. Brönsted, loc. cit.

<sup>21</sup> F. Chem. Soc., 127 (1925), 1371, 1385; 129 (1927), 2539 and 2554. *Structures et Activités chimiques*, Paris, 1926, page 135 et seq.

<sup>22</sup> Rec. trav. chim., 42 (1923), 718.

<sup>23</sup> Chem. and Ind., 42 (1923), 43.

<sup>24</sup> See also G. N. Lewis, *Die Valenz und der Bau der Atome und Moleküle*, Braunschweig, 1927, Seite 158.

<sup>25</sup> Z. physik. Chem., 108 (1924), 185; 118 (1925), 299.

<sup>26</sup> F. Chem. Soc., 126, 2282, 2873; 127, 2444 and elsewhere.

<sup>27</sup> E. Müller, loc. cit. Compare also E. Hückel, Z. Elektrochem., 34 (1928), 546. .

of the Sörensen  $p_H$  scale within which it is, therefore, not catalysed by  $H^+$  and  $OH^-$ , and proceeds with great velocity (half-change period = 29 minutes at 25°).

Lowry and his co-workers have now shown that mutarotation does not take place either in dry pyridine or in dry cresol, but on the other hand that in a mixture of both solvents it proceeds more rapidly even than in water.

The solvent in which the reaction takes place must accordingly be of an amphoteric nature—e.g., water or a mixture of cresol and pyridine—it must be both proton-donor and proton-acceptor. The suitability of the solvent to facilitate the reaction is thus dependent upon its chemical nature; the solvent is not merely a medium, it takes part in the reaction as a transfer catalyst.

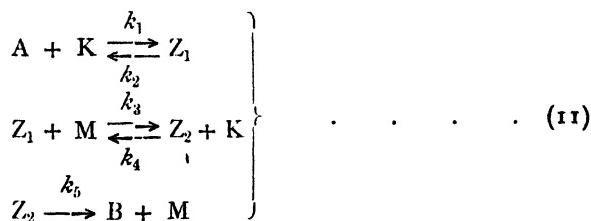
Lowry divides solvents into three groups:—

(a) *Amphoteric solvents* which act as complete catalysts.

(b) *Solvents which are either acids or bases.* They are of themselves not catalysts but they act in the presence of auxiliary catalysts.

(c) *Inactive solvents* which are neither acids nor bases.

Lowry's theory of the catalysis of the reaction  $A \rightarrow B$ , which supposed two intermediates, can be generalised in the following scheme, which is at the same time an extension of scheme (3):—



By analogy with what has already been said with reference to the simple scheme (3), we can now say:—

If the substrate A is a (weak) acid the catalyst K must be a base, the medium M a (weak) acid or an amphotelyte.

If the substrate A is a (weak) base, the catalyst is an acid, the medium a (weak) base or an amphotelyte.

If the reaction proceeds in the pure medium M *without* catalyst (*c.f.* the term  $k_w$  of equation (1)), the medium M is a base and an acid. Such a reaction necessarily requires an amphoteric medium. If the medium acts in the first part of the reaction as an acid it is in the second part a base, and *vive versa*. The terms acid, base, and amphotelyte are used here in the modern sense. If this reaction is to take place, according to scheme (11) proton-acceptor and proton-donor must simultaneously contribute to the effect on the substrate A.

Finally it follows that the intermediate body  $Z_1$  is of the nature of a salt or ion, but the intermediate  $Z_2$  must be an uncharged molecule or a bi-polar molecule (*Zwitterion*).

If, now, we interpret scheme (11) kinetically we can, according to the relative values of the velocity constants (*i.e.* whether the intermediates  $Z_1$  and  $Z_2$  are van't Hoff or Arrhenius intermediate bodies) distinguish the following three limiting cases in all of which the concentration of the medium can be introduced as a constant quantity amongst the velocity constants:—

*Case (i).* The formation of  $Z_1$  decides the velocity:—

$$\frac{d[B]}{dt} = k_1[A][K] \quad \dots \quad \dots \quad \dots \quad (12)$$

*Case (ii).* The decrease of  $Z_1$  or the formation of  $Z_2$  determines the velocity:—

$$\frac{d[B]}{dt} = k_3[Z_1] = k_3 \frac{k_1}{k_2} [A][K] = k_3 G_1[A][K] . . . (13)$$

*Case (iii).* The decrease of  $Z_2$  is the deciding factor:—

$$\frac{d[B]}{dt} = k_5[Z_2] = k_5 \frac{k_3[Z_1]}{k_4[K]} = k_5 \frac{k_3 k_1}{k_4 k_2} [A] = k_5 G_2 G_1[A] . . . (14)$$

Case (iii) must be rejected because it leads to an equation which is incompatible with the experimental result expressed by equation (4). On the other hand, proposals (i) and (ii) accord to an equal degree with the experimentally ascertained equation (4). The kinetic consequences are thus again ambiguous. We must therefore consider which of the two cases (i) or (ii) is the more probably right.

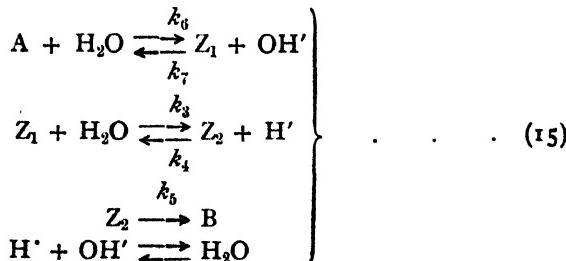
Lowry himself assumes that the first of the stage reactions of scheme (11) is strongly endothermic, the second equally strongly exothermic, and, further, that the two parts of the reaction are coupled by reason of the fact that the necessary energy to promote the first reaction is provided by the energy of the second process. Therefore, it is implied that Lowry favours proposal (12) in which  $Z_1$  is a van't Hoff intermediate. From the purely kinetic standpoint the latter proceeds more readily as the reaction  $Z_1 + M \rightarrow Z_2 + K$  is more rapid in comparison than  $A + K \rightarrow Z_1$ . The relatively large velocity of the first reaction follows in fact with some probability, by reason of the instability of the intermediate body  $Z_1$  and the large surplus of the solvent molecule  $M$  in comparison with the catalyst molecule  $K$ .

We will, however, now discuss the Lowry mechanism for the case when the reaction  $A \rightarrow B$  proceeds along the kinetic lines of a simultaneous reaction.

As a concrete example, let us take the hydrolysis of the ethers  $R_2O$ . The hydrolysis of the typical ethers is only catalysed by acids<sup>28</sup> but very reactive ethers can be hydrolysed by water alone.<sup>29</sup>

According to scheme (11) of the catalysed reaction,  $K$  represents then the hydrogen ion (which for simplicity we will write as  $H^+$  not  $OH_3^+$ —a matter of no importance for the moment) and  $M$  is the water molecule. Moreover  $Z_1$  is the oxonium ion  $R_2OH^+$  and  $Z_2$  the undissociated oxonium hydroxide  $R_2OH(OH)$ , i.e. its *Zwitterion*.

For the hydrolysis carried out by water alone and uncatalysed we have:



which according to scheme (11) coexists with the acid hydrolysis. The last reversible reaction of scheme (15) as is known by experience goes so rapidly that the equilibrium is always maintained.

\* Cf. A. Skrabal and O. Ringer, *Monatsh. Chem.*, 42 (1921), 9; A. Skrabal and A. Schiffrer, *Z. physik. Chem.*, 99 (1921), 290; A. Skrabal and H. Airildi, *Mobath. f. Chem.*, 45 (1924), 13.

\*\* A. Skrabal and M. Baltadschiewa, *Monatsh. f. Chem.*, 45 (1924), 39 and 95.

We have then for the uncatalysed reaction again three cases to consider :

*Case (i).* The formation of  $Z_1$  determines the velocity :

$$\frac{d[B]}{dt} = k_6[A] \dots \dots \dots \quad (16)$$

*Case (ii).* The decrease of  $Z_1$  or the formation of  $Z_2$  is decisive :

$$\frac{d[B]}{dt} = k_3[Z_1] = k_3 \frac{k_6}{k_7} \cdot \frac{[A]}{[OH']} = k_3 \frac{G_3}{w} [A][H'] \dots \dots \quad (17)$$

*Case (iii).* The decrease of  $Z_2$  is the determining factor :

$$\frac{d[B]}{dt} = k_5[Z_2] = k_5 \frac{k_3}{k_4} \frac{[Z_1]}{[H']} = k_5 \frac{k_3}{k_4} \cdot \frac{k_6}{k_7} \cdot \frac{[A]}{[H'][OH']} = k_5 \frac{G_2 G_3}{w} [A] \quad (18)$$

Since in the case of the uncatalysed reaction the equation is :

$$\frac{d[B]}{dt} = k_w[A] \dots \dots \dots \quad (19)$$

case (ii) is excluded, but on the other hand cases (i) and (iii) are consistent with equation (19) and are therefore possible.

The velocity equation for the simultaneous reactions is as follows :

$$\frac{d[B]}{dt} = k_w[A] + k_a[H'][A] \dots \dots \dots \quad (20)$$

and with this our equations (12), (13), (14), (17), (18) and (19) should coincide. The comparison of these equations as well as of the equations which can be deduced for the three simultaneous reactions (1) gives two possibilities :

*Possibility (a).* The intermediates of Lowry's mechanism are of the van't Hoff type and equations (12) and (16) serve in the case of all simultaneous reactions; the measured velocity is that at which the first of the intermediates ( $Z_1$ ) is formed. This assumption is the simplest, for in this way the interpretation of the time relationship is uniform for all cases of the change  $A \rightarrow B$ .

*Possibility (b).* The intermediate bodies are of the Arrhenius type. If the velocity with which the first intermediate  $Z_1$  reacts be measured in the case of the reaction accelerated by acids or bases, equation (13) is of value. In the case of an uncatalysed reaction, however, the velocity is determined by the transforming of  $Z_2$  according to equation (18). This possibility is not at all definite for it depends upon whether the reaction is catalysed or uncatalysed, but it lies well within the region of possibility. We merely observe that catalysed reactions are more rapid than uncatalysed ones. The more sluggish a process is, the more readily can one detect the equilibria which determine the velocity of the whole. In the case of rapidly catalysed reactions we are concerned only with the first equilibrium (that which leads to  $Z_1$ ), in the case of the more sluggish uncatalysed reaction the equilibrium leading to formation of  $Z_3$  is also involved.

The ambiguity of the time relationship is therefore not done away with, if a secondary effect is attributed to the time relationship (1) for the reaction.

From the purely kinetic standpoint I see on consideration only one criterion, and that is the suitability of assumption (a) according to which the formation of the intermediate body is the determining factor as to velocity. For experience shows that the reaction velocity of most of the acid and base catalysed processes can be better represented if one substitutes in equation (1) in addition to H-ion and OH-ion the corresponding terms for the proton-donors and -acceptors. With the exception of the equilibrium

of the typical pseudo-acids the dissociation equilibria of the acids and bases and the hydrolysis equilibria of their salts are established with the greatest rapidity. If then assumption (b) is correct the dissociation equilibrium of the acids and bases are added to the above-mentioned equilibria of the intermediate bodies  $Z_1$  or  $Z_2$ ; we can deduce the effect of the former alone, from the effect of the hydrogen ion concentration equilibrium, by which also the equilibrium concentration of the hydroxyl ions is given.

An example will make this clear. Let us assume a reaction  $A \rightarrow B$  catalysed by acids, which takes place in solution of the weak acid HS and its salts. For greater simplicity let it be assumed that it takes place under the "buffer condition," i.e. that the concentration of  $H^+$  is very small in comparison with that of acid and salt. We have then the following equilibrium:

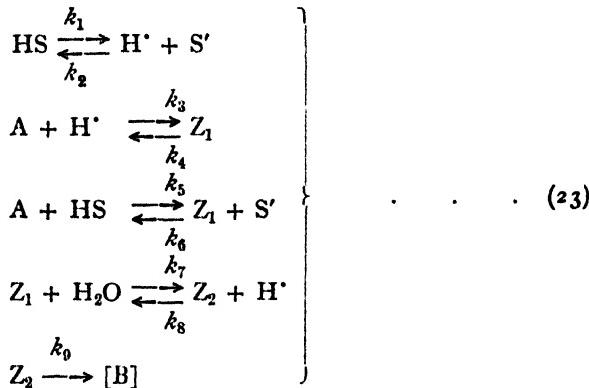


and for  $[H^+]$  the equation

$$[H^+] = \frac{k_1 [HS]}{k_2 [S']} = \delta \frac{[HS]}{[S']} \quad . \quad . \quad . \quad . \quad . \quad (22)$$

wherein  $\delta$  is the dissociation constant of the acid HS,  $[HS]$  the concentration of the weak acid and  $[S']$  that of its salt.

The stage-by-stage reactions of the catalysis mechanism are according to Lowry, as follows:



If we make assumption (a), whereby  $Z_1$  is a van't Hoff intermediate, we get the kinetic equation of two simultaneous reactions:

$$\frac{d[B]}{dt} = k_3[H^+][A] + k_5[HS][A] \quad . \quad . \quad . \quad . \quad . \quad (24)$$

wherein  $H^+$  is defined by equation (22).

If on the other hand we make assumption (b), whereby  $Z_1$  is an Arrhenius intermediate, we find only the time equation of a simple reaction (without simultaneous reactions) in which we can define the concentration of  $Z_1$  in the equation of the critical reaction (i.e. that one which determines the velocity of the whole) in an arbitrary manner by the equilibria:

$$\begin{aligned} \frac{d[B]}{dt} &= k_7[Z_1] = k_7 \frac{k_3}{k_4} [H][A] = k_7 \frac{k_5}{k_6} \frac{[HS]}{[S']} [A] \\ &= k_7 \frac{k_5}{k_6} \cdot \frac{k_2}{k_1} [H^+][A] = k_7 \frac{k_5 k_1}{k_4 k_2} \frac{[HS]}{[S']} [A] \quad (25) \end{aligned}$$

It is of no great importance that the process  $A \rightarrow B$  can be somewhat more readily written by introducing into the equation all the proton-acceptors and proton-donors; for a better conformity with the time relationship must necessarily go hand in hand with the multiplication of the constants. The fact, however, that reactions, such as the catalysis of nitramide measured by Brönsted, are known which cannot be portrayed by the three terms of equation (1) (and for whose representation it is necessary to introduce, in addition to  $H^+$  and  $OH^-$ , the other proton-acceptors and proton-donors present in the solution) suggests that assumption (a) alone is appropriate. The fact that several reactions can be sufficiently accurately described by means of the three terms of equation (1) proves that in aqueous solution hydroxonium-ion is the most effective proton-donor and hydroxyl-ion the most effective proton-acceptor.

From the form of the velocity equation of the underlying reactions of acid and basic catalysis we must conclude that the first stage of the reaction, the formation of the intermediate body  $Z_1$  of Lowry's scheme is the important one in determining the velocity of catalysed and uncatalysed reactions.

The observations which Lowry has made with regard to the intramolecular character of the changes involved in the molecular transformation  $A \rightarrow B$  lead necessarily to the same conclusion. We are concerned in this case with the individuality and delicacy of the reaction mechanism, which can hardly be given expression in our kinetic reaction scheme.

Lowry's theory is an electrolytic theory of catalysis, according to which the proton-donor attaches itself to one of the points of attack of the changing molecule, immediately thereafter the proton-acceptor attaches itself to the other, and there flows through the molecule from the one to the other point of attachment an electric current in the form of migrating valency electrons. The explanation of the short life or instability of the intermediate compounds is to be found in the rapidity with which these events follow upon one another.

The Lowry theory consists in a re-animation of the conception of A. de la Rive and H. E. Armstrong,<sup>30</sup> according to which, in order to bring about a chemical reaction, it is essential to use a system analogous to a galvanic chain. "Die ganze Materie ist ein elektrisches Phänomen." In these words of H. A. Lorentz it is implied that the transformation of matter, the chemical reaction, is also an electric phenomenon.

### Summary.

An explanation of acid and basic catalysis has been sought in the theories which have been advanced from the standpoint of chemical kinetics.

In all theories it is assumed that acid and basic catalysed reactions proceed through the formation of unstable intermediate bodies.

It has been shown that, from the kinetic point of view, two types of unstable intermediate bodies are postulated: the Arrhenius type which are in chemical equilibrium with the initial materials and the van't Hoff type which is not controlled by this equilibrium. The latter is of greater instability than the former.

It has been shown that Lowry's electrolytic theory of catalysis accords best with experimental facts, and that the intermediate bodies postulated by this theory are of the van't Hoff type.

<sup>30</sup> See J. W. Mellor, *loc. cit.*, page 273 *et seq.*

## HOMOGENEOUS CATALYSIS.

### GENERAL DISCUSSION.

ON PAPERS PRESENTED TO THE SOCIETY ON 28TH AND  
29TH SEPTEMBER, 1928.

#### PART I. GENERAL RELATIONS.

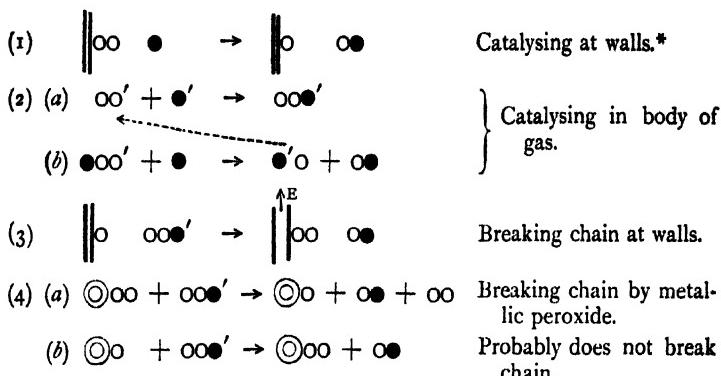
**Mr. A. Egerton** referred to several points that had arisen, particularly as they affected the phenomenon of combustion in which he became interested when starting on an investigation to find out how "anti-knocks" prevented "knocking." The work might be summarised by saying that it led to the discovery that anti-knocks act as inhibitors of the preliminary, and comparatively slow, processes of oxidation of the hydrocarbons. Professor Callendar and his associates, also Professor Moureu in France, arrived at a similar conclusion. He thought all were agreed on many of the essential points, but it seemed to him there were two differences in their points of view. The view held by Callendar was (1) that combustion occurs at liquid or solid nuclei which form the essential reaction centres, and (2) that organo-metallic anti-knocks owe their efficacy (as Dr. Mardles said in his paper) "to the reducing action of the colloidal metal formed by the thermal decomposition at the surface of nuclear particles." Mr. Egerton wished to say a few words on both these points, as it seemed to him that they touched on the two really important features of the discussion, *viz.* :—(1) the nature of the primary centres which initiate reaction, and (2) the circumstances which affect the life of an active molecule.

His view was (1) that reaction occurred "in the body of the gas" in centres of high energy and proceeded by a reaction chain mechanism, and (2) that "anti-knock" inhibitors acted by stopping the chains and that they were already in a state of oxidation when they were effective.

Before discussing these two rather different points of view, he wished to explain what they<sup>1</sup> meant by a certain sentence: "whatever the precise nature of the surface catalysis, we think that reaction in the body of the gas does not occur till the oxygen is presented to the fuel molecules in something the same active state as it exists on the surface. This is occasioned by formation of oxidation products such as peroxides which thus become autocatalysts. When sufficient catalyst is present and diffusive influences are not too prevalent, reaction may become rapid enough to set up centres of ignition in the body of the gas. Surface catalysis avoids the formation of these peroxides and in fact destroys them, and so conditions that promote surface combustion tend to raise igniting temperature. There is thus an essential difference in surface combustion and combustion in the body of the gas, though really the processes are in both cases catalytically similar"—the action was the same, the effect opposite.

<sup>1</sup> Egerton and Gates, *J. Inst. Pet. Tech.*, 13, 284, 1927.

The following scheme indicated what was meant. (Double line signified metal; black, fuel; white, oxygen) :-



The similarity in the action (1) and 2(b) was indicated, but the effect was different as in 2(b) the product had greater energy. Again there was similarity between the actions (3) and 4(b), but he thought the effect would be different as 4(b) would not necessarily break the chain; the energy could not be dispersed, as no doubt it was at the walls. On the other hand 4(a) as it divided the energy of the product between 3 instead of 2 molecules would more likely be effective. The above was perhaps a very crude representation of affairs, but it might be of some use in defining the problems which arose.

Returning to the first point of difference, he said he agreed that small particles of "fuel" were much more readily oxidised at an interface; if liquid nuclei were present, peroxidation occurred then at the surface rapidly and no doubt peroxides became concentrated in the droplet. He thought that reaction spread out chainwise from such active, freshly formed molecules released from the surface in the vapour phase and was only checked by (1) lack of concentration of reactants, (2) deactivation at wall, (3) molecules which could exchange energy with and react with the active products, and lastly by (4) a certain proportion radiating their energy away, giving rise perhaps to chemiluminescence.

If the "anti-knock" were *only* to be of influence on minute droplets or particles of fuel, he found it difficult to understand how the combustion of gaseous mixtures (such as those of CO and air) could be so greatly influenced by traces of inhibitors such as iron carbonyl and how inhibitors were as effective when added in the vapour state as if introduced dissolved in the fuel. Yet here he would agree that fog formation was in general an accompaniment of the process of inhibition of oxidation in the vapour state, though these fogs seemed to him to be the result of oxidation (of fuel and also of inhibitor) rather than to be essential to the initiation of the oxidation process. Did the fog particle first form by condensation of a reactant (as a cluster on an ion for instance) and then become exposed to oxidation, or did preliminary oxidation take place amongst the molecules of vapour, after which ions or nuclei of some sort were formed, upon which less active products gradually collected, these, being influenced by neighbouring molecules, being more readily oxidised? He had held the latter view, but

\* The metal held very firmly to one adsorbed oxygen, weakening the bond between the two oxygens.

there was still need for further experiment. It was only a question of the particle being essential or not, as it was perfectly clear that, once there, oxidation occurs more readily.

Mr. Tietz in the Balliol Laboratory had been investigating the photochemical oxidation of acetaldehyde vapour (at 25°)—and he was studying at his (Mr. Egerton's) suggestion the action of some inhibitors on the reaction. With certain substances such as iron carbonyl and diethyl selenide a very pronounced period of induction was obtained, during which a fog was formed, which then gradually subsided; only when the fog commenced to disperse did oxidation commence. He thought the fog formed by reason of the gradual growth of particles of stable oxidation products of the inhibitor, upon which oxidation products of the aldehyde collected. But as the reaction was a chain reaction, the initial inhibition of the chains occurred in the vapour phase; otherwise, if it were a question of supplying a surface at which the reaction should be stopped, a particle of ZnO for instance, should do as well as one of iron oxide. At any rate it seemed that the finer the particles, the greater the inhibition; some recent engine results with a volatile and a non-volatile anti-knock seemed to be explained by the fact that in one case—the more effective—the anti-knock was vaporisable, while in the other case it could only be dispersed. If this view were incorrect, he thought the reverse should occur.

The initiation of a reaction was a very interesting point. If it were only molecules of high energy, thermally activated, that were needed, why for instance did hydrogen and oxygen react more readily if a trace of moisture were present. Semenoff had shown that an exceedingly small number of active centres were necessary to set going a chain reaction which might culminate in explosion. Semenoff assumed, for the purpose of his calculation, that these centres were thermally activated—

$$N_0 = Ae^{-E/RT}.$$

$\tau$  was the life of the active centre and the numerator was the Arrhenius formula; a very small number of such centres might be required. He wondered, however, whether thermal activation alone were necessary. He pointed out that water was essential to get some chain reactions going (Na + Cl<sub>2</sub> for instance). Water assisted an atom (for example Hg) to assume a metastable state,<sup>2</sup> and it seemed probable that the primary reacting molecules, although possessing high translational energy, must also undergo some corresponding internal disturbance. Was it necessary that this should go so far as ionisation (or that it should be influenced by the field of an ion)? Although such activity would be expected if ionisation occurred, it seemed doubtful whether ionisation was essential. The evidence in the case of phosphorus (where only one ion in eight millions was produced), though not completely satisfactory, was against such a view.

This led up to Mr. Hinshelwood's very interesting discovery as to the behaviour of nitrogen oxides on the hydrogen-oxygen reaction. He thought that the combustion of hydrocarbons provided an almost exactly similar case; peroxides were formed (he referred to the work of Professor Callendar and his associates, Professor Moureu, Messrs. Rideal and Brunner, and Egerton and Gates.) If Mr. Hinshelwood had not already done so, he had intended to suggest that these were cases of chain catalysis, such as those to which Semenoff had drawn attention.

<sup>2</sup> Wood, *Phil. Mag.*, Aug., 1928.

The pressure of the  $\text{NO}_2$ , at which the reaction proceeds, appeared to be independent of temperature, when once a certain temperature had been reached, which, according to Semenoff's reasoning, might indicate that this was a case of explosion resulting from some chain reaction in which the  $\text{NO}_2$  takes part, supplying the necessary reaction centres. The peroxide underwent a reaction such that a number of thermally activated reaction centres,  $\text{N}_0$ , are produced sufficient to promote the chains which go on in the surrounding gas. Semenoff had shown that when  $\text{N}_0$  attained a certain value, the reaction chain mechanism auto-accelerated and explosion could occur. Inhibitors (such as anti-knocks) could thus act by stopping the chains<sup>3</sup> or by delaying the formation of the peroxides; this was probably the same thing, as, although the latter might be initiated at the surface, they were probably augmented by chain reaction. He thought the essential point of the discussion was that certain reaction centres were clearly necessary.

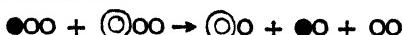
The higher limit of effective  $\text{NO}_2$  concentration might perhaps be explained by some reaction product acting as inhibitor, in something the same manner as Dr. Mardles had found to occur in the case of carbon bisulphide; though in that case he could not see how it could be actually the  $\text{CS}_2$  molecule itself which acted as inhibitor.

He did not think it was realised how sensitive ignition was (under certain circumstances) to change of oxygen concentration. A change of 75 to 80 per cent. of  $\text{N}_2$  would raise the igniting temperature of hexane, for instance, over  $100^\circ\text{C}$ , and it was in these regions only that the effect of inhibitors was noticeable.

The behaviour of the explosion of a hydrocarbon in an igniting pot in mixtures richer in oxygen was very different. A considerable delay occurred before ignition, which was then much more violent and rapid, an occurrence which was perhaps akin to Hinshelwood's observations with  $\text{NO}_2$ . There was still much to learn about these reactions; he had tried to indicate some of the points where perhaps they were still rather in the dark.

Referring to the other point made by Callendar, with which he did not entirely agree—"that the organo-metallic anti-knock acts as a colloidal metal and reduces the peroxides," Mr. Egerton remarked that Dr. Mardles had drawn attention to the action of metals in stopping the glow—in the first place, the "glow" or chemiluminescence was only incidental—an accompaniment of the chain reactions, in the second place the metals inhibited action by stopping the chains and their relative effect depended mainly on the extent and state of the surface exposed. In the case of the anti-knocks, a single atom of lead had to delay the reaction of  $10^5$  molecules; he did not see how it could do this by merely reducing a single oxidised molecule in a droplet. It must either remove a reaction centre or break a chain. Potassium did it well; if potassium why not zinc, if it were merely a question of reduction.

He felt that, both quantitatively and qualitatively, there was considerable evidence against the view of the protection of the nuclear drop against oxidation by the colloidal metal dispersed in it. Those metals which were effective were capable of being peroxidised and of being re-peroxidised if reduced so that they could be rendered effective again. Whether some such action as



was really taking place (the energy being divided amongst 3 products) as he had postulated following Moureu's scheme of negative catalysis, or not, he

<sup>3</sup>Cf. Bäckström's communication (p. 603).

was not yet certain, but something of the sort took place; this might account for the fact that peroxides may behave in some cases as positive and sometimes as negative catalysts depending on oxygen concentration.

However, on the whole the views he had attempted to discuss seemed to him to be gradually converging.

**Professor W. E. Garner** remarked that Mr. Hinshelwood in a very interesting study of trace catalysis, had come to the conclusion that the lowering of the ignition temperature of mixtures of hydrogen and oxygen by nitrogen peroxide was due mainly to a thermal process. The Dixon reaction, the catalysis of carbon monoxide by water or hydrogen, was perhaps the best known case of trace catalysis, and here also experimental work had shown that the catalysis was to a large extent thermal in character. Catalysis of a chemical nature was very probably not entirely absent. The study of the total radiation (mainly infra-red) from the flame of carbon monoxide and oxygen to which varying percentages of hydrogen were added, had given the results represented in the figure.<sup>4</sup> The radiation fell, as the percentage of hydrogen was added, in three stages. The decrease in the

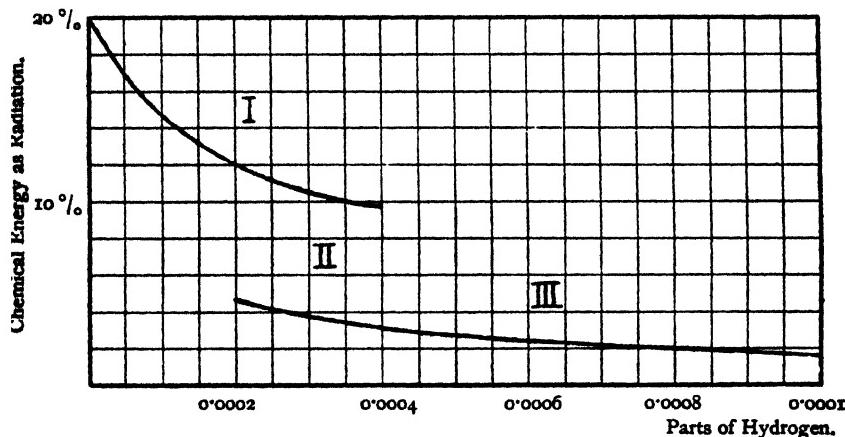
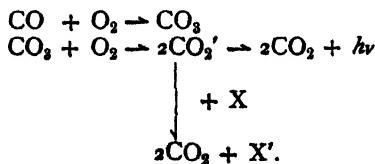


FIG. 1.

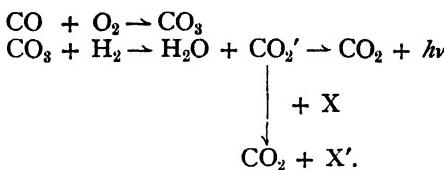
radiation emitted was accompanied by an increase in speed over portions I. and III. The sudden fall at II. was not accompanied by any very marked change of speed. The decrease in infra-red radiation in regions I. and III. and the change in speed were interrelated. The conservation of energy within the system which occurred on addition of hydrogen must lead to catalysis of a thermal character (energo-thermic catalysis, or catalysis by collisions of the second kind).

It was concluded that in region I. of the curve, there occurred physical catalysis of the type:—



<sup>4</sup>From experiments by Mr. F. Roffey, Bristol University. In region II., any value for the radiation could be obtained which lies between the upper and lower curves.

The sudden fall in the radiation which occurred at constant speed of flame was attributed to chemical catalysis, or else to the onset of a second type of physical catalysis. The chemical catalysis might be provisionally represented by



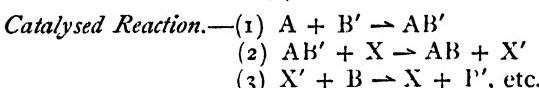
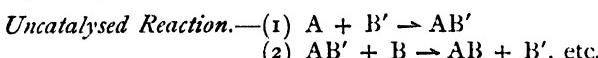
Region III. was then a range of combined chemical and physical catalysis.

The speed of flame-composition curve was similar in character to the above figure.<sup>5</sup>

The type of physical catalysis involved was the activation of the molecule of the catalyst by the internal energy of the products of combustion and, since  $\Delta R \propto \sqrt{H_2}$ , they concluded that the transference of energy might occur between  $\text{CO}_2'$  and  $\text{H}^+$  or  $e^-$ .

Although this type of catalysis might be of rare occurrence in chemical change, it was advisable that its presence be tested for in other cases of positive catalysis, both homogeneous and heterogeneous.

Positive and negative catalysis were explainable on this mechanism. Taking the general case :—



$\text{AB}'$  might be activated by virtue of its internal or kinetic energy. Confining one's attention to internal energy both of  $\text{AB}'$  and  $\text{X}'$ , whether  $\text{X}$  were a positive or a negative catalyst appeared to depend on the facility with which internal energy is transferred on collision. This was highly specific. Where  $\text{X}'$  transferred its energy to  $\text{B}$  more rapidly than did  $\text{AB}'$ , one might have positive catalysis. In the reverse case, negative catalysis. In only very exceptional cases would positive catalysis be anticipated, since the number of stages for the catalysed process was greater than for the uncatalysed reaction.

**Mr. Hinshelwood** said that Professor Bone had shown that spectroscopic differences existed between the ultra-violet emission from dry and moist gases on explosion, indicating two distinct mechanisms occurring side by side for this reaction. Did Dr. Garner's explanation confirm this view?

**Dr. Garner** replied that the work was in general agreement with the observations of Professor Bone. The above, however, led to a clearer analysis of the mechanism.

**Dr. H. F. Coward** said that like Mr. Hinshelwood, he had been interested in Professor H. B. Dixon's discovery of the influence of traces of nitrogen peroxide on the ignition temperatures of hydrogen and methane; for there were small amounts of nitrogen peroxide in the gaseous products of detonation of certain solid explosives, and these hot products might

<sup>5</sup> See *Ind. and Eng. Chem.*, 20, 1008, 1928.

therefore be more dangerous when mixing with the atmosphere of a coal mine than had been suspected hitherto. Mr. F. J. Hartwell and he had started some experiments, for the Safety in Mines Research Board, to test this point by determinations of the limits of inflammability of methane and hydrogen in the presence of nitrogen peroxide. The lower limit of hydrogen, upward propagation of flame, was but little affected, if at all, by various small amounts of nitrogen peroxide; nor was the lower limit of methane, downward propagation. This suggested that Professor Dixon's observations were based on some surface phenomenon, a view which Mr. Hinshelwood seemed inclined to take. The lower limit of methane, upward propagation of flame, did, however, show an appreciable decrease (from 5·24 to 5·00 per cent. methane) in the presence of a suitable small amount of nitrogen peroxide. The decrease was not, however, nearly so great as might be expected from the large ignition temperature differences observed by Professor Dixon.

**Professor M. Polanyi** said in reference to a remark in Mr. Hinshelwood's paper, that there could be no doubt of the formation of molecules out of free atoms by means of three-body collisions. To question this would involve doubting the possibility of dissociation of molecules by collision, as the existence of any dissociation of this sort proves also the existence of the inverse process, *i.e.*, the formation of molecules by three-body collisions. In fact the calculation given by Herzfeld<sup>6</sup> for the velocity of molecule formation by three-body collisions was identical with the calculation of the speaker<sup>7</sup> for the dissociation of molecules by collision, the result being applied by Herzfeld to the inverse reaction.

**Mr. Hinshelwood** said that Dr. Polanyi seemed to have received from his paper the impression that he criticised the "Dreierstoss" theory adversely. He ought to explain that he had only referred to certain *experimental* attempts to verify it or disprove it as inconclusive. From the theoretical point of view Dr. Polanyi was on strong ground.

**Dr. Bernard Lewis** (*National Research Fellow, U.S.A.*) remarked that reference had been made in several papers to active nitrogen. He said it was doubtful whether certain phenomena in active nitrogen could be considered as belonging to homogeneous catalysis. For instance let them consider the effect of the presence of small quantities of oxygen. Herzberg<sup>8</sup> and he (Dr. Lewis)<sup>9</sup> had found not only that pure nitrogen in an ordinary moist vessel shows an intense afterglow, but that pure nitrogen or nitrogen containing say 0·2 per cent. oxygen (which under ordinary conditions produces an intense afterglow) in a thoroughly baked-out vessel gave rise to no afterglow whatsoever. The experiments of Herzberg and the speaker showed conclusively that the appearance or non-appearance of the afterglow was dependent on the condition of the surface of the containing vessel. For instance the admittance of enough water vapour to cover the surface immediately caused a restoration of the glow. If the afterglow formation were due to a process following the combination of two nitrogen atoms, the action of the walls was easily understood. Bonhoeffer and Kaminsky<sup>10</sup> had shown that if this view was correct, the union of two nitrogen atoms did not require a collision with a third body. The experiments with oxygen just cited supported this as well as certain calculations, testing a theory of the temperature coefficient, which quantitatively accounted for the temperature coefficient of the afterglow between room temperature and the temperature

<sup>6</sup> K. F. Herzfeld, *Z. Physik*, **8**, 132, 1922.

<sup>7</sup> M. Polanyi, *Z. Physik*, **1**, 337, 1920.

<sup>8</sup> *Z. Physik*, **46**, 878, 1928.

<sup>10</sup> *Z. physik. Chem.*, **127**, 385, 1927.

<sup>9</sup> *J. Amer. Chem. Soc.*, in press.

of liquid air. This theory assured that only nitrogen atoms which possessed small velocities (or more exactly, those which possessed velocities below a certain value) resulted in combination.

**Professor Ch. Moureu (Paris)** said that he had read with interest the communication of Professor Dhar. He noted some lines in which the latter seemed to be claiming a certain degree of priority, since he indicated, as being his own, some results which they (Professor Moureu and his collaborators) had published as early as 1921 and which they had extended since then in several publications (stabilisation of various organic products, especially turpentine, fats, and india-rubber). Professor Dhar referred on page 568 to a remark that he had made, quite incidentally (among other reflections suggested by the experiments which he was then describing), in 1921.

It was important to observe that Professor Dhar's remark (interesting though it was) in the form presented in his paper of 1921 (as in the present report) could not be employed as the basis of a theory explaining facts of autoxidation catalysis, as the phrase was now understood. On the other hand, Professor Moureu and his colleague had formulated a proposition of very broad significance since it included all the results of experiments on autoxidation catalysis up to the present day. The essential condition for a substance to be an autoxidation catalyst was, not that it be a reducing body (as claimed by Professor Dhar) but that it be oxidisable by the primary peroxide  $A[O^2]$ . The difference between the two propositions was fundamental, since there were non-reducing bodies which were autoxidation catalysts.

For instance, di-sodium phosphate,  $Na_2HPO_4$ , was not accepted as an easily oxidisable body in the sense indicated by Professor Dhar, although it was oxidisable by high potential peroxide,  $A[O^2]$ , in the case of certain autoxidations, such as the autoxidation of furfrol. Furthermore, oxygen was not an oxidisable body in Professor Dhar's sense, but, nevertheless, in certain autoxidations, it could become oxidisable, e.g., in phosphorus autoxidation, where one could see the formation of ozone and one knew that in that case the oxygen itself could play the part of anti-oxygen. Moreover, one could find, in the long catalogue of catalysts that they had established, numerous bodies which, contrary to the opinion of Professor Dhar, were autoxidation catalysts, without being what are commonly called reducing agents (diphenylamine, potassium iodide, iodoform, etc.).

Further they had shown that, in a molecule all the parts of which were oxidisable, that part alone possessed catalytic properties which was oxidisable under the conditions of the experiment. If one suppressed the oxidisability at that stage in the experimental condition, one suppressed the catalytic power of the molecule, although the rest of the molecule were itself still oxidisable. Thus, for example, consider diphenyl sulphide ( $C_6H_5)_2S$ , which was an energetic anti-oxygen towards the furfrol autoxidation; if it were transformed into sulphone ( $C_6H_5)_2SO_2$ , the catalytic property disappeared. The catalytic property in the case of the sulphide, was localised in that part of the molecule which was oxidisable under the conditions of the experiment (by the  $A[O^2]$  peroxide); they had saturated the S atom with oxygen by changing the molecule to sulphone, so that there was now nothing oxidisable by  $A[O^2]$  peroxide, and the catalytic property had disappeared.

It seemed to him (Professor Moureu) that their proposition had been very fruitful; it had enabled them to found a whole doctrine from which a great many consequences had proceeded, and which had been used not only by themselves, but also by numerous other workers.

**Dr. W. P. Jorissen (Leiden) (communicated later)**, said that Professor Dhar had mentioned two of his (Dr. Jorissen's) recent publications on

induced oxidation<sup>11</sup> but had forgotten to cite two others,<sup>12, 13</sup> published in 1897 and 1925 respectively. In both, the simultaneous oxidation of sodium sulphite and sodium arsenite solutions was studied quantitatively, using two different methods. The result of the experiments was to establish that both substances fixed the same quantity of oxygen. Moreover the figures in both papers showed clearly that the oxidation of the sulphite was retarded very much by the presence of the arsenite, as confirmed by Dhar in 1921.<sup>16</sup>

That "all the negative catalysts (in slow oxidations) were good reducing agents" or that they were "readily oxidised" was a generalisation which seemed to go too far, as would be observed when studying, for instance, the publications of Bigelow,<sup>14</sup> Titoff,<sup>15</sup> and others, on the oxidation of sodium sulphite and that of Centnerszwer<sup>16</sup> on the oxidation of phosphorus.

It was true, however, that many of those negative catalysts were more or less easily oxidised. In several cases, under favourable circumstances, their oxidation was "induced" to such an extent by that of the sodium sulphite or another "inductor" that the "acceptor" fixed as much oxygen as the "inductor."

**Professor N. R. Dhar** (*communicated later*) said that the point raised by Professor Moureu was readily settled, since he (Professor Dhar) had published his results and views in 1921.<sup>17</sup>

Professor Moureu, in his publications had always referred to the paper of Mittra and Dhar.<sup>18</sup> It would appear that his publication in 1921<sup>17</sup> had escaped the attention of Professor Moureu.

He added that the terms oxidising and reducing agents were used relatively; nitrous acid, ozone, etc. behaved both as oxidising and reducing agents and diphenylamine, potassium iodide, etc. were reducing agents because they could be oxidised under suitable conditions.

He had not mentioned Dr. Jorissen's paper of 1897,<sup>12</sup> since it seemed to be concerned only with the applicability of Schönbein's law in the induced action of sodium arsenite in the presence of sodium sulphite.

With regard to Dr. Rideal's remarks on ionisation in oxidation reactions, he wished to point out that the substances to be oxidised were in intimate contact with each other and, hence, the ions generated from the primary exothermal chemical change could be readily taken up by the other substances. If the ionisation could be measured before a good deal of recombination occurred, this phenomenon would be observed in most exothermal chemical reactions. In the majority of cases of induced oxidations the primary change was an exothermal chemical reaction.

The interesting experiments recorded by Gill, Mardles and Tett on "Phosphorescence and Autocatalysis"<sup>19</sup> were in entire accord with his (Prof. Dhar's) views on negative catalysis and the mechanism of induced reactions and chemiluminescence.<sup>20</sup>

**Dr. H. Bäckström** (*Princeton*) referring to Dr. Rideal's paper on negative catalysis, in which he mentioned the existence of a large group

<sup>11</sup> *Rec. Trav. chim.*, **42**, 855 (1923), **43**, 582 (1924).

<sup>12</sup> *Z. physik. Chem.*, **23**, 667 (1897).

<sup>13</sup> (With C. van den Pol), *Rec. trav. chim.*, **44**, 805 (1925).

<sup>14</sup> *Z. physik. Chem.*, **26**, 493 (1898).

<sup>15</sup> *Ibid.*, **45**, 641 (1903).

<sup>16</sup> *Ibid.*, **26**, 1 (1898).

<sup>17</sup> *Proc. K. Acad. Wetensch., Amsterdam*, **29**, 1023, 1921.

<sup>18</sup> *Z. anorg. Chem.*, **122**, 146, 1922.

<sup>19</sup> *Trans. Far. Soc.*, **24**, 574 (1928).

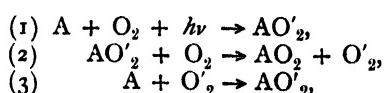
<sup>20</sup> *Z. anorg. Chem.*, **173**, 125, 1928.

of reactions in which the inhibitor acted by removing a positive catalyst, said that, in actual fact, with the exception of a few simple cases of acid catalysis, there was not at present known a single example of that kind. The oxidation of sulphite solutions was definitely a chain reaction, and the experiments on the copper-catalysed reaction which were mentioned in his (Dr. Backström's) contribution to this discussion, showed that the action of the copper consisted merely in increasing the number of chains started in a given time, whereas the inhibitor acted by breaking the chains, quite independently of how those chains were started. It was also significant that no attempt had ever been made, by Titoff or anybody else, to establish such a correlation between inhibitory power and capacity for combining with copper as would be required on the Luther-Titoff theory.

Dr. Rideal discussed in his paper the mechanism of the reaction between benzaldehyde and oxygen, and of similar autoxidation reactions. He (Dr. Backström) had given a detailed discussion of these reactions in his two papers in the Communications from the Nobel Institute. He wished to emphasise, however, that there did not seem to be any reason, experimental or theoretical, for assuming that ions played an important part in the mechanism of these reactions, as was done particularly by Professor Dhar. Even in the slow combustion of phosphorus, in which the extent of ionisation was certainly greater than in any other autoxidation reaction, the number of ions actually formed was less than 1 in a million molecules reacting; and Busse's work<sup>21</sup> on that ionisation had shown that it was an altogether secondary phenomenon. No ionisation had been observed in the oxidation of benzaldehyde. Professor Dhar's observation, communicated in his contribution to this discussion, that the oxidation of sulphite gave rise to ionisation, was very interesting in this connection but its significance could not be judged until the experimental data had been published. It should be remembered, also, that from the point of view of the necessary energy, ionisation was a much less probable event than the excitation, to an "optical" energy-level, of a molecule of one of the reactants, particularly of the oxidisable substance. It followed directly from the photochemical experiments that such excitation was sufficient to start a reaction chain. In his papers he had tried to show that, on the present theory of chemiluminescence, one should expect such excitations to take place in those reactions.

**Dr. J. A. Christiansen** (*Copenhagen*) (*communicated later*) remarked : (1) It had recently been customary to distinguish between material or chemical chains (*Stoffketten*) and energy or physical chains (*Energieketten*). This distinction seemed to him somewhat inadequate, since (a) no chain was possible without transfer of energy from some active product-molecule to some reactant molecule, and on the other hand (b) no chain of reactions could be propagated without material transformations. It seemed to him therefore more logical to speak *generally* of chain-reactions and when considering *special* cases to specify the supposed chain mechanism.

(2) Dr. Rideal stated in his paper (p. 573) that a chain-mechanism represented by the following equations :



"does not permit of a rising velocity under isothermal reactions." This statement was not correct, as it was not at all impossible, and in some cases

<sup>21</sup> Busse, *Ann. Physik*, **82**, 873 and **83**, 80 (1927).

it was even probable, that the excited molecules formed in reactions (1) and (3) had sufficient energy to activate two molecules instead of one. The reason was that  $\text{AO}_2'$ , as compared with  $\text{AO}_2$ , contained not only the energy of activation (represented by " $h\nu$ "), but also the ordinary heat of reaction, which was in some cases very great.<sup>22</sup> This possibility and its consequences was discussed in a paper by Kramers and the writer some years before Semenoff's very interesting and valuable work appeared.

**Professor Ch. Moureu (Paris)** said that Mr. Rideal had given a general account of the problem of negative catalysis which revealed his clear-sightedness and his wide knowledge of the subject. He wished to congratulate Mr. Rideal upon it.

He would have a few words to say on the theory of catalytic autoxidation but these would probably come more appropriately in connection with Dr. Christiansen's paper. For the moment he would confine himself to accentuating the great importance of that branch of negative catalysis of autoxidation.

As a result of the experimental work which he had carried out during more than ten years past with numerous collaborators, and more particularly with M. Dufraisse, a certain number of general facts began to emerge clearly; it might be useful, in order to render clear the discussion on that phenomenon, to mention the principal advances made.

*The great generality of the phenomenon of the negative catalysis of autoxidation. The two inverse catalyses.* When they began their work on this subject, one would have thought, judging from the work already published, that the phenomenon was of an exceptional character, and only concerned with certain rare substances. On the contrary, they had demonstrated that what they had named anti-oxygenic action, far from being rare, was a most widespread general phenomenon, not only in the great diversity of autoxidisable substances which might be protected against oxidation, but in the infinite variety of catalysts.

At the present time, as a result of their experiments, they believed they were correct in formulating the following double proposition:

(a) All oxidation by free oxygen might be influenced by the use of suitable catalysts.

(b) Under appropriate conditions, an immense majority of substances could act as anti-oxygenic catalysts. In practice, what was found to be exceptional was not, as was believed before their researches, the occurrence of anti-oxygenic action, but rather the absence in an autoxidation of all anti-oxygenic impurities.

It might not be superfluous if at this point he gave an idea of the experimental bases on which he depended in enunciating this double proposition, which would have appeared absurd a few years ago.

They had created a mass of means of investigation (material, experimental arrangements, methods of work, etc.) which had allowed them to accumulate rapidly a considerable number of measurements. Thus, among some thirty communications which they had published up to the present, one frequently found that more than ten thousand measurements of oxygen absorption had been made in connection with only one paper. In addition, they had experimented on the most varied autoxidisable substances, and the number of catalysts whose action had been tried amounted to many hundreds. Furthermore they were systematically passing in review the different families of substances and those containing different radicles.

Contrary to all expectation, they had established the fact that the same

<sup>22</sup> Compare for instance Bäckström's papers in *Medd. från Nobel Institutionen*.

catalyst might, according to the experimental conditions, *diminish* or, on the other hand, *accelerate*, the phenomenon; in other words, it might play an *anti-oxygenic* part or a *pro-oxygenic* part. One could not therefore call a certain substance anti-oxygenic and another pro-oxygenic. One must assign to each the generic term "Autowidative catalyst," the positive or negative sign of the catalysis depending less on the nature of the catalyst than on the circumstances in which it was brought into action. He would confine himself to mentioning two examples of this *close relationship of these two inversely related catalytic actions*.

Whilst a trace of phosphorus oxybromide prevented the autoxidation of benzaldehyde, the same substance accelerated more than a hundredfold the velocity of oxidation of styrene. The second example which he might quote, concerned a product of great industrial importance, indiarubber. The ageing of this substance, which was due to autoxidation, might be considerably hindered by antioxygenic agents. If pyrogallol were used as catalyst, it had been shown<sup>23</sup> that, according to the sample of indiarubber used, the ageing might be either slackened or accelerated.

If one now considered the consequences of the negative catalysis of autoxydation in other domains, one was bound to concede its great importance.

In all ages men had been concerned, and for a long time in a very empirical manner, to avoid the harmful effects of oxidation. They had made use for this purpose of different methods, of which some were actually true anti-oxygenic catalyses. Since beginning their researches, they had been able to discover, in a review of the literature, only a few cases of the practical utilisation of anti-oxygenic action, the phenomenon having been overlooked. But at the present time, there were many who, attracted by their publications, had applied their methods in a great number of different directions, and during the last few years a number of important results had followed. Thus, in their earliest publications (June 1921 and January 1922) they indicated a large number of applications in which, according to their experiments, anti-oxygenic action might render service. The following was a brief account of some cases of the utilisation of anti-oxygenic catalyses.

Firstly, in the laboratory, one might very frequently protect autoxidisable substances without difficulty. They might emphasise the interesting fact that stabilisation by an anti-oxygenic agent might amount to more than simple protection of a quantity of material; in preventing the autoxidative formation of peroxides, the initiation of certain harmful accessory reactions brought about by these peroxides was also prevented. Thus, for example, stabilised acrolein gave much better yields when treated with Grignard reagents, and essence of turpentine was converted in better yield into camphor.

In industry, apart from the case of essence of turpentine which he had just mentioned, numerous axtoxidisable substances might be protected with ease. He need mention only those they had indicated in 1921; hydrocarbons, aldehydes, fats, and indiarubber. The application of anti-oxygens to the preservation of indiarubber was just at present acquiring great importance.

At times the most unexpected and far-reaching consequences appeared. This was what had happened in the working of internal combustion engines, where one had the problem of anti-detonating agents, to which he proposed to return in another communication.

<sup>23</sup> Pelizzola, *Giorn. Chim. Ind. Appl.*, 6, 89, 1924.

With regard to Biology, in order to realise the consequences of autoxidative catalysis, one had only to recall that life itself was above all an autoxidation, and that, in addition, the materials of which living bodies were composed abounded in substances which they had found to possess the properties of catalysts of autoxidation. Indications on this subject would readily be found in their publication of 1921 and in many of their later communications.

**Dr. H. J. Emeléus** said that in studying the spectra of some of the phosphorescent flames described by Dr. Mardles and his collaborators the surprising observation was made that in the case of ether, acetaldehyde, propionaldehyde, and hexane, the spectrum was the same, consisting of a series of bands between 4930-3385 Å. This was totally different from the spectra of the hot flames of these compounds, in all of which the Swan bands and "water bands" are prominent. At present the light emission could not be associated with any definite stage of the complex chemical changes involved, nor was its molecular origin known, but from the point of view of the light emission (which might, however, be a secondary process) the four flames were identical. The simplest explanation was that the luminosity was due to the oxidation of acetaldehyde, which was known to be produced in each case. The differences in the action of inhibitors on the flames of hexane and acetaldehyde might be due to the inhibition in the case of the former of the process by which the acetaldehyde was produced.

**Professor Ch. Moureu (Paris)** in connection with the paper of Dr. Mardles and his collaborator, which was a continuation of the interesting publications on combustion carried out under the direction of Professor Callendar, referred to researches he and his colleagues had carried out in an allied field.

(1) The rational development of their study of anti-oxygenic actions led them to consider the working of explosion motors and especially the phenomenon known as *knock*. As early as 1925 at the Congrès de Chimie Industrielle they had presented their first publication on this subject and this was followed by a series of others.<sup>24</sup> They had concluded definitely that the action of anti-detonators was anti-oxygenic, and they had tried to look carefully into the mechanism of the action of these bodies. On the other hand they had visualised, as a result of their investigations, a mechanism of knock itself which had been proposed at the same time (only a few days before) in England by Professor Callendar and in which an important rôle was attributed to the autoxidation peroxides which were formed in the compression phase.

(2) He would draw the author's attention to the suggestive comparison they (Professor Moureu and his colleagues) had established between what they had called the Perkin's cold flame phenomena and the tendency of a fuel to "knock." As they had shown, the fuels came out in the same order whether they were tabulated according to their tendency to give the Perkin's cold flame or their tendency to knock.<sup>25</sup>

(3) He asked Dr. Mardles and his colleagues to explain their conception of the mechanism of the action of inhibitors. They assumed, as did Professor Moureu, that there was destruction of peroxide, but it did not follow

<sup>24</sup> Congrès de Chimie Industrielle Paris, 1925; *Chemical Rev.*, 3, 1926, 113; *Compt. rend.*, 184, 1927, 413; *Chimie et Ind.*, 17, 1927, 531; *ibid.*, 18, 1927, 3; *Ann. de l'Office National de Combustibles Liquides*, 2, 1927, 233; *Chem. and Ind.*, 47, 1928, 819.

<sup>25</sup> *Ann. Off. nat. comb. Liq.*, 2, 1927, 233.

from their paper whether the destruction was effected stoichiometrically or catalytically.

(4) When the catalyst was present in small proportion, as in the case when anti-detonants of the nature of lead tetraethyl were used, the action could manifestly only be catalytic. In such a case he suggested that Dr. Mardles and his colleagues should adopt their (Professor Moureu's and his colleagues') mechanism of antioxygenic action.

**Dr. Mardles** in reply to Professor Moureu said they considered in the presence of metals, iron from iron carbonyl, lead from lead tetraethyl, nickel from nickel carbonyl, etc., catalysis at the surface of the metal was responsible for the removal of activated primary peroxides or moloxides in a gaseous system.

Experiments in the laboratory had shown that the above metal derivatives inhibited the formation of active oxygen in precisely the same manner as the corresponding metals which remained unoxidised. The exact function of the metal was at present unknown; lead, iron, nickel, thallium and platinum usually exerted a greater effect than aluminium, zinc magnesium or bismuth, whilst in most instances the metal caused the slow combustion to begin at a lower temperature although the formation of active oxygen was inhibited.

With organic compounds such as benzene, aniline, etc., it was easy to demonstrate that they acted by simply reacting with the peroxides, being autoxidised to phenol and other oxidation products which could be isolated.

The interesting relationship pointed out by Professor Moureu between Sir W. Perkin's experiments on luminous slow combustion and the tendency of a substance to detonate confirmed the view that peroxidation was the cause of detonation.

Carbon bisulphide was an apparent exception because although peroxidation and luminous slow combustion occurred, it could, nevertheless, act as an inhibitor of detonation. This anomaly could best be explained by the difference in character between the carbon bisulphide moloxide and those of hexane, heptane, etc., which were violent explosives.

## PART II. INTERMEDIATE ADDITION-COMPOUNDS AND CHAIN REACTIONS.

**Professor A. W. Porter** said he was rather surprised that no reference had been made, when dealing with condensed systems, to the collateral information that could be gained from a knowledge of the vapour pressures of the components. It was well known that the law of mass action held only in the case of perfect gas mixtures; in other words, in strictness it never held good at all. It was also well known that for condensed systems a nearly exact relation could be obtained by replacing the concentrations in the "mass-action" equation by the vapour pressures of the components. Thus instead of  $c_1^{n_1}c_2^{n_2} \dots = K$ , which failed to apply, one might write  $\pi_1^{n_1}\pi_2^{n_2} \dots = K$  and a nearly exact equation for equilibrium was thereby obtained. It would be advantageous therefore if every experiment on the changes in the system were accompanied by a simultaneous determination of vapour pressures.

In recent papers he had shown how suitable equations could be obtained for representing vapour pressures.<sup>1</sup> These equations were obtained by the

<sup>1</sup> *Trans. Far. Soc.*, 24, 343, 405 (1928).

use of Margules' theorem which restricted one in the choice of empirical equations, definitely forbidding many of the equations which had hitherto been used for the purpose. If for the sake of illustration he took the simplest possible equation thereby determined, the vapour pressures of one of the components in a binary condensed system might be written

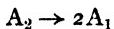
$$\pi_1/\Pi_1 = \mu_1 e^{\beta(\mu_2)^2}$$

where  $\pi_1$  = vap. pressure for the molar fraction  $\mu_1$   
 $\Pi_1$  = " pure component  
and  $\beta$  = a constant. Also, for the second component

$$\pi_2/\Pi_2 = \mu_2 e^{\beta\mu_1^2}$$

where  $\beta$  was the same constant as before. From the form of Margules' equation,  $\beta$  was obviously the coefficient of the mutual action between the components.

Supposing further that one considered the simplest reaction



the rate of dissociation was not  $\kappa\mu_2$  as it would be for a perfect gas system, but  $\kappa_2\mu_2 e^{\beta\mu_1^2}$  and the final equilibrium state was given by

$$K = \frac{\kappa_2\mu_2 e^{\beta\mu_1^2}}{\kappa_1\mu_1^2 e^{\beta\mu_2^2}}$$

The exponential terms were the so-called *activity coefficients*. It was noteworthy that the activity coefficient for  $A_2$  depended primarily upon the molar fraction of  $A_1$  although of course  $\mu_1$  could be written  $1 - \mu_2$ . In whatever way it was written, its existence depended upon the mutual action between the components.

If one added a third substance (a catalyst) it changed the vapour pressure of the two components and thereby indicated a change in the reaction. In a paper on the vapour pressures of mixtures<sup>2</sup> he extended Margules' theorem to the case of ternary systems. The corresponding values for the vapour pressures in terms of  $\mu_1$ ,  $\mu_2$ ,  $\mu_3$  were shown to be

$$\pi_1/\Pi_1 = \mu_1 \text{Exp. } \{\beta_1\mu_2^2 + (\beta_1 - \beta_2 + \beta_3)\mu_2\mu_3 + \beta_3\mu_3^2\}$$

$$\pi_2/\Pi_2 = \mu_2 \text{Exp. } \{\beta_2\mu_3^2 + (\beta_2 - \beta_3 - \beta_1)\mu_3\mu_1 + \beta_1\mu_1^2\}$$

Even if the third body (for which a similar equation held) underwent no change it was thus seen that it would modify the changes of the other two. Equations derived logically from Margules' equation became very complicated as the number of components increased. If the vapour pressures were however obtained experimentally it might be possible to fit to them empirical equations, of permissible form and of sufficient accuracy, from which inferences might be made in regard to the nature of the reactions taking place both with and without the presence of the catalyst. He was not aware that this had ever been done.

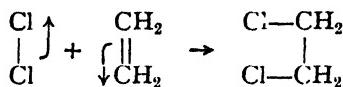
When the expressions which he had found for vapour pressures were examined there was no difficulty in understanding the powerful effects which even very small quantities of a catalyst might have. For example, the same equation which represented the vapour pressures for a  $\text{CaCl}_2$  solution in water throughout the whole range of solubility, also represented, without any change of constants, the so-called absorption of water in  $\text{CaCl}_2$  when the water was present in minute quantities. In this latter region the activity of the  $\text{CaCl}_2$  runs up to many thousands of times its more usual values. He proposed to discuss these abnormal effects more fully at an early date. They obviously had an important bearing on this subject.

<sup>2</sup> *Trans. Far. Soc.*, 15, iii., 75, 1919.

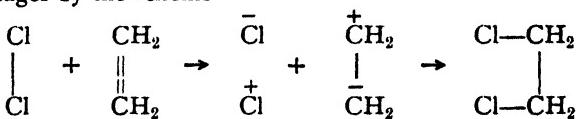
The catalytic action of glass, etc., was intimately connected with the same explanation, though of course it took one into the region of heterogeneous systems. The glass exerted mutual action on the neighbouring gaseous or liquid system and its activity explained on the same lines might be very great indeed.

Reference to Part III. of his papers referred to above (1928) would call attention to the close connection between the  $\beta$  coefficients and the latent heat of dilution. This last effect also depended upon the mutual action between molecules.

**Professor Lowry** said that during the second part of the Discussion a very able account had been given by Professor Kendall of the part played by intermediate addition-compounds in the hydrolysis of esters, and an equally able account had been given by Professor Boeseken of a physical process of catalysis by dislocation, but without excluding the alternative of compound-formation in suitable cases. It was important to maintain both views. Thus, when an ester was hydrolysed, the acid or alkaline catalyst actually contributed one component of the final addition-product (namely hydrogen or hydroxyl) whilst the other component (hydroxyl or hydrogen) was easily obtained from the solvent. In such cases it was incredible that the catalyst failed to form a definite addition-compound with the ester. On the other hand, in Norrish's experiments on the combination of ethylene with chlorine or bromine, the catalyst was merely a polar compound, such as water, cetyl alcohol, or stearic acid, which played no similar specific part in this reaction, and it might indeed be merely a surface of glass or silica. In such cases it was equally obvious that the catalysis depended on a mere "dislocation" and not on the formation of a definite addition-compound. In particular, the formation of ethylene chloride or bromide depended on a displacement of electrons, which was more likely to be unsymmetrical than symmetrical, and might therefore be represented in a single stage by the scheme



or in two stages by the scheme



The catalyst could then act merely by creating a polar environment or field of force which destroyed the normal symmetry of the system and thus determined the direction in which the flow of electrons must take place.

**Mr. W. F. K. Wynne-Jones** remarked that Professor Kendall claimed that there was a parallelism between his results and Lowenherz's rule, that for ester hydrolysis in acid solutions the speed was greatest for the esters of the strongest acids. However this rule broke down when the esters of the strong mineral acids were considered, the hydrolysis of those substances being almost insensitive to hydrogen ions.

It would perhaps be of interest to see whether those esters formed hydrates; but, even if Professor Kendall's conclusions were valid, it was difficult to see how the substitution of an ester hydrate for the ester itself could explain the mechanism of catalysis any more than the hypothetical existence of ion hydrates could explain the phenomena of ionisation.

**Professor Ch. Moureu (Paris)** said with regard to the report of Dr. Christiansen :—

(1) M. Dufraisse, his (Professor Moureu's) principal collaborator and friend, and he, wished to consider particularly the chemical point of view of the phenomenon, and to consider the physical, energetical repercussion, only when such consideration was indispensable.

They had proposed an energetic theory (action of the catalyst on the concentration of equilibrium of the active molecules), just because it seemed to them simple and practical, but they did not hold to it entirely, and they were ready to accept any other energetic theory which might be established by the discussions going on.

Nevertheless, they wished to say that they had not formulated their own energetic theory without mature consideration: before its publication it had been largely discussed with eminent physicists and physical chemists, and they insisted on the fact that the theory accorded with the principles of thermodynamics and was not in opposition thereto, as some had been led to believe. Concerning this, he drew attention to the discussions printed in the *Comptes Rendus de l'Académie des Sciences*<sup>3-4</sup>, and the article of René Dubrisay which would be published shortly.<sup>5</sup> For those who wished to have a short review of Dubrisay's conclusions he had a few notes.<sup>6</sup> From

<sup>3</sup> Francois Perrin, *Comptes rendus*, 184, 1927, 1121.

<sup>4</sup> Ch. Moureu and Ch. Dufraisse, 185, 1927, 1545; 186, 1928, p. 196.

<sup>5</sup> *J. Chim. Phys.*

<sup>6</sup> *On the possibility of displacement of equilibrium between active and ordinary molecules by a catalyst.*—We can define catalysts *theoretically* in the following manner: we give the name of catalyst to any substance which, introduced into a chemical system, modifies its speed of evolution, while remaining subject to the following two conditions:—

(a) We can at all times introduce the substance into the system or remove it from the system without the manifestation of any energy phenomenon.

(b) The substance remains unchanged at the end of the reaction.

For every catalytic agent satisfying this definition, we readily establish, as an immediate consequence of Carnot's Principle, that in a reversible reaction the introduction of a catalyst can in no case modify the value of the parameters defining the state of final equilibrium.

However, it is important to note that the preceding definition is purely theoretical and, in particular, does not apply with complete rigour in reality to the substances which we agree to regard as catalysts. Nevertheless the theorem holds if, according to A. Job, we modify the definition as follows:—

We assign the name of catalyst to every substance which, introduced into a system in a definite physical state, modifies its speed of evolution, provided that its mass be very small with respect to the mass of the substances constituting the initial system, as well as relative to the mass of the final products of the reaction.

This definition applies to the ordinary catalysts and the theorem enunciated retains its value and its generality *if precautions are taken in its application*. However it does not seem legitimate, as some have wished, to put Carnot's Principle in opposition to the interpretation of catalysis (proposed as a consequence of the theory of Arrhenius) upon active molecules. In fact, a substance which exerts a catalytic action in the reaction  $A \rightarrow B$  can certainly be used, conformably to the definition, in very small quantity with respect to the mass of the initial molecules A or final B, its quantity remaining, however, finite or even large relative to the mass of the active molecules  $A'$ : the equilibrium  $A \rightleftharpoons A'$  can then be displaced by the introduction of the catalytic agent.

M. René Dubrisay has, in an article which is going to appear in the *Journal de Chimie Physique* and in a communication made before "La Société de Chimie Physique," established for liquids, the relation

$$iRT \frac{dc'}{c'} + \frac{\epsilon}{m'A'} \left( \frac{\delta f}{\delta \epsilon} \right) = 0$$

where  $c'$  = concentration of the active molecules.

$\epsilon$  = mass of the catalyst.

$m'A'$  = mass of the active molecules.

$f$  = molecular potential of the active molecules.

$R$  = constant of gases.

$T$  = absolute temperature

$i$  = coefficient of ionisation.

As in real liquids it is possible that  $\frac{\delta f}{\delta \epsilon}$  may be different from 0, we see that when  $\frac{\epsilon}{m'A'}$  is

## GENERAL DISCUSSION

the formula, this author had established that the concentration of active molecules in liquids could be greatly modified by the presence of relatively small quantities of a catalyst.

Consequently, there was no need to look to any other energetic theory. In particular, the theory of chain reaction, to which they were not opposed, was not indispensable. They thought that experiments only, and not a theoretical discussion, should be decisive as to the choice of a theory.

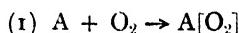
(2) They wished to draw special attention to the point that, whatever energetic theory be adopted, one must necessarily at some time or other conceive a chemical mechanism, which could satisfactorily explain the experimental results now accumulated. It could not be contested, for example, that it was totally insufficient to be satisfied by saying that the catalyst poisons something, or forms a varnish on something, or that it breaks something (a chain, for example).

Thus it followed that every explanation of auto-oxidation catalysis must have two parts, which were of equal importance : an energetic conception, and a chemical mechanism.

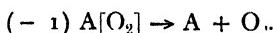
Consequently, although as said above, they did not wish absolutely to maintain their energetic conception of the phenomenon (although it was legitimate and rational) and preferred to leave to others the care of discussing it thoroughly, on the other hand, they wished to draw attention to the interest of their chemical mechanism, which adequately explained the already observed facts ; it had already, and with success, acted as guide, not only for their own experiments, but also for those of numerous other workers. Up to date, no other mechanism had been suggested, to their knowledge, to replace it. They suggested, therefore, that this mechanism be adopted till another more satisfactory one be found.

**Dr. Christiansen** (*communicated later*) said that although, in common with all chemists interested in the problems in question he assuredly appreciated highly the experimental work of Professors Moureu and Dufraisse, he could not agree with their theoretical discussion of the experiments. He would try to explain why.

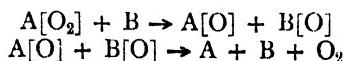
Professors Moureu and Dufraisse had proposed a definite chemical mechanism of the oxidation and inhibition. This mechanism seemed indeed to him to be probable up to a certain point, but it could not possibly explain the experimental facts (quite apart from those found by Backstrom) if it was not supplemented by the assumption of some chain mechanism. To show this, one might assume with Moureu and Dufraisse that the first step in oxidation of (e.g.) benzaldehyde could be represented by



where  $A[O_2]$  represented an unstable "primary peroxide." If this be granted one must also assume the possibility of exactly the opposite process :—

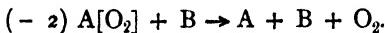


To explain the effect of the anti-oxygen B (the inhibitor) Moureu and Dufraisse assumed the following two reactions,

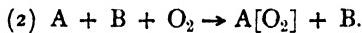


great  $\frac{dc'}{c}$  is finite and can even be very great : in other words it is not legitimate to say that the introduction of a catalyst cannot modify the concentration of equilibrium of the active molecules.

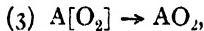
thereby indicating that the substance B took part in the de-activation of  $A[O_2]$  without being used up, i.e., they considered B as a true catalyst for the reaction  $A[O_2] \rightarrow A + O_2$ . One might write for the sake of brevity:—



Now whatever the mechanism of this catalysing action be one must also assume the possibility of exactly the opposite reaction



Finally, of course, one must assume a transformation



and it was the velocity of this, the formation of stable  $AO_2$ , which one desired to know.

As  $A[O_2]$  had been assumed to be unstable, i.e. to have a short life in the mixture it was certainly permissible to assume that its concentration became *stationary* immediately after starting the reaction. This gave:

$$\frac{d}{dt}C_{A[O_2]} = 0 = k_1 C_A \cdot C_{O_2} + k_2 C_A \cdot C_B \cdot C_{O_2} - C_{A[O_2]}(k_{-1} + k_{-2} C_B + k_3).$$

The velocity  $v$  was

$$v = C_{A[O_2]} \cdot k_3.$$

From these equations one readily deduced

$$v = k_3 C_A \cdot C_{O_2} \frac{k_1 + k_2 C_B}{k_{-1} + k_{-2} C_B + k_3}.$$

In that equation  $C_A \cdot C_{O_2} \cdot \frac{k_1}{k_{-1}}$  must be equal to the *equilibrium* concentration of  $A[O_2]$  if no other reactions than ( $\pm$  1) took place and similarly  $C_A \cdot C_{O_2} \cdot \frac{k_2 \cdot C_B}{k_{-2} C_B}$  represented the equilibrium concentration of  $A[O_2]$  if no other reactions than ( $\pm$  2) took place. As, however, this equilibrium concentration must be independent of the way in which the molecules  $A[O_2]$  were formed it was seen that

$$\frac{k_1}{k_{-1}} = \frac{k_2}{k_{-2}} = \frac{k_1 + k_2 C_B}{k_{-1} + k_{-2} C_B}$$

Consequently

$$v = k_3 C_A \cdot C_{O_2} \frac{\frac{k_1}{k_{-1}}}{1 + \frac{1}{\frac{k_1}{k_{-1}} + \frac{k_2}{k_{-2}} C_B}} = k_3 C_A \cdot C_{O_2} \frac{\frac{k_1}{k_{-1}}}{1 + \frac{1}{\frac{k_1 + k_2 C_B}{k_{-1} + k_{-2} C_B}} C_B}.$$

Here only the last factor depended on  $C_B$ , and it was easily seen that it must always increase with  $C_B$ . According to this picture the velocity could consequently never be decreased by addition of B and it was thus seen that the mechanism proposed was not sufficient to explain the experimental results of Moureu and Dufraisse.

That it became sufficient when some chain effect was assumed had been shown so often by different authors that he thought it unnecessary to repeat the proof here.

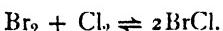
**Dr. Jorissen** (*Leiden*) (*communicated after the meeting*) referring to Dr. Bäckström's paper, as well as to Professor Dhar's communication in Part I., said that he had published a survey of the quantitative results obtained previous to 1904 in the "Chem. Weekblad," Vol. I. (1904). Since then some more results had been obtained. For instance, a sodium

antimonite solution (containing sodium bicarbonate) which was not oxidised in an atmosphere of oxygen, oxidised when sodium sulphite was added and both substances fixed the same quantity of oxygen.<sup>7</sup>

In the presence of a phosphate buffer, sulphite and mannite absorbed each the same quantity of oxygen; so did sulphite and indol (without a buffer), sulphite and dimethylaniline (with phosphate buffer). Also other acceptors were studied.<sup>8</sup> In most cases the hydrogen ion concentration of the solutions appeared to have a considerable influence, which had already been observed by S. I. Vles<sup>9</sup> in the case of the simultaneous oxidation of sodium sulphite and sodium arsenite solutions. But, whether the acceptor (present in excess) would fix the same quantity of oxygen as the inductor, or not, seemed to depend on other circumstances also.

Backström came to the conclusion—in agreement with Christiansen's theory of negative catalysis—that the rôle of the inhibitor (also in thermal reactions) consisted in the breaking of reaction chains and that the mechanism, by which the chains were broken, was probably an induced reaction between the inhibitor and one of the reactants. His assumption was that in the presence of an inhibitor the oxidation of one sulphite ion did not always induce that of another but sometimes induced the oxidation of an inhibitor molecule. Now, in the cases mentioned above, in which the sulphite and the inhibitor fixed the same quantity of oxygen, one would have to suppose, it would seem, that the oxidation of *each* sulphite ion induces the oxidation of an inhibitor molecule.

**Mr. T. W. J. Taylor** (*communicated later*) said that in deducing of the chain-length in the presence of the inhibiting bromine, Professor Polanyi used the ratio of the bromine concentration to the total halogen concentration. It seemed to him possible that account should be taken of the equilibrium :—



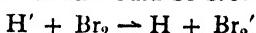
Indications existed that in this equilibrium the concentration of BrCl was considerable, and if these indications were correct, the presence of the BrCl would magnify the inhibiting effect of the bromine. In a collision with an H-atom a molecule of BrCl would give HCl + Br, and thus instead of the presence of a certain number of Br<sub>2</sub> molecules there might be twice that number of inhibiting BrCl molecules.

It was further possible that in the unexplained influence of temperature on the inhibition, the shift of the above equilibrium on change of temperature might be playing some part.

**Professor Garner** then asked Professor Polanyi in connection with his mechanism for the retardation of the reaction between hydrogen and chlorine, whether he had demonstrated that HBr is actually present in the products. He assumed that the chain mechanism was broken by collision of hydrogen atoms with bromine molecules according to the equation



Was it not possible that the chain would be broken by



without formation of HBr? It would seem that Professor Polanyi had a possibility in his reaction of testing whether the negative catalysis was a physical or a chemical process.

<sup>7</sup> W. P. Jorissen and C. van den Pol, *Rec. Trav. chim.*, **43**, 582 (1924).

<sup>8</sup> These experiments (made with A. H. Belinsante) will be published *in extenso* elsewhere.

<sup>9</sup> *Rec. Trav. chim.*, **46**, 743 (1927).

**Professor M. Polanyi** replying to the questions of Professor Garner and Mr. T. W. J. Taylor respectively said, (1) that the physical process  $H' + Br_2 \rightarrow H + Br'$  was not possible, because the activation of an H-atom (to the first term of the Balmer-series) required more than 200 calories, which were not available, as the reaction  $Cl + H_2 \rightarrow HCl + H$  yielded practically no energy at all. (2) He could find in the literature no data indicating the existence of a compound  $ClBr$  in gaseous mixtures. But even if such a compound did exist, he could not assume that it was formed in the course of the very short time (0.05 sec.) during which the mixture of  $Cl_2$  and  $Br_2$  existed in his experiments, especially if the very low pressures of the components (0.1 - 0.01 mm.) were considered.

**Professor Giordani** (*Naples*) referred to the contribution of Professor Böseken, wherein he had said that, according to his researches, the theory of intermediate compound formation could not explain why a catalyst accelerates a given reaction. He had pointed out that sometimes reacting substances formed very stable and well-defined addition compounds with products that showed very little catalytic influence, while other products, giving unstable addition compounds, were most effective.

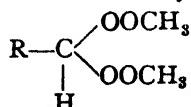
Many years ago he (Professor Giordani) had pointed out—on the basis of old experiments of Bayer and Villiger, and of exhaustive researches carried out by Professor Kendall and his co-workers—that compound formation must take place with the appropriate groups of molecules in order to be effective.<sup>10</sup>

In the case of ester formation, or hydrolysis, one could imagine some compound formation of the oxonium type. One knew in this instance that the tendency to give addition compounds and their stability, were largely dependent on the nature of the groups previously attached to the oxygen atom.

It was easy to imagine that the addition (brought about through subsidiary valencies) must have some influence on the stability of the reacting substance, weakening the principal valency bonds and enhancing the reactivity.

The fact that well-defined crystalline addition compounds failed, in many instances, to catalyse the reaction was clearly understood since, according to the above hypothesis, in order to loosen the valency bonds addition must take place at a definite place. If, in the case of nitrobenzoyl chlorides, the addition was brought about through  $NO_2$  groups and not through the chlorine atom, it was clear that no influence could result in the Friedel-Craft reaction. Similar results were obtained by Professor Bakunin.

He added that a thorough examination was needed in such cases. When studying, in collaboration with Professor Bakunin, the mechanism of the Perkin-Oglialoro synthesis, he found compound formation between nitro-benzaldehydes and acetic anhydride, quite different from those obtained between the same products in the presence of a particular catalyst. These latter products (very stable and well defined) were diacetates of the type—



and had no influence in the reaction.<sup>11</sup> But the addition compounds formed without catalysts, and probably of the oxonium type, were much more efficient for synthesis.

<sup>10</sup> *Boll. Soc. Nat. Napoli*, 32, 18, 1918.

<sup>11</sup> *Gazz. Chim. It.*, 46, 77, 1916.

He thought, therefore, that the old theory was not yet superseded and could be further utilised along the lines that he had just merely summarised.

In the second part of his report Professor Böseken purported to bring forward experimental evidence against the view expressed by Arrhenius that the catalyst may produce a decrease of the energy of activation  $A$ , in the formula—

$$\ln k = - \frac{A}{RT} + B.$$

Two years ago he (Professor Giordani)<sup>12</sup> had pointed out that kinetic measurements did not always give the true value of  $A$ , and that, therefore, the fact that, on addition of catalyst, the temperature coefficient rose was not contradictory to Arrhenius' view.

Considering the reaction  $M \rightarrow P$ , which proceeded according to the formula—

$$\frac{d[M]}{dt} = k[M],$$

and a catalyst  $N$  acting through the formation of a highly reactive addition compound  $MN$ , it was clear that—

$$[MN] = \frac{K}{[N]} [M]$$

and therefore, if the velocity of reaction (constant  $k_1$ ) for the addition compound were sufficiently high, one could write

$$\frac{d[M]}{dt} = \frac{d[MN]}{dt} = \frac{k_1 K}{[N]} [M].$$

In other words the rate at which  $M$  reacted was practically coincident with the rate at which  $MN$  was transformed.

In that case the ratio  $\frac{k_1 K}{[N]}$  took the place of the velocity constant  $k$  and

$$\frac{d \log k}{dT} = \frac{d \log k_1}{dT} + \frac{d \log K}{dT} = \frac{A + Q}{RT^2}$$

$Q$  being the heat of the addition compound formation.

This observation was very useful whenever one undertook experimental research on the energy of activation by means of kinetic measurements.

Furthermore, it seemed likely that the addition of catalyst to a reacting molecule, if it would otherwise be effective in activating the reaction, might give a negative action by reason of a sort of steric hindrance which prevented reaction.

In reply to Professor Lowry, Professor Giordani emphasised that in his remarks he had made no reference to electrons owing to the actual lack of definite and universally accepted knowledge of intramolecular mechanisms.

But many years ago,<sup>13</sup> on the basis of the classical theory of Lorentz, he had supposed that the photochemical effect resulted in the resonance of valency electrons originated by impinging radiation. This resonance would loosen valency bonds, when the frequency of activating radiation equalled the characteristic frequency of the valency electrons.

In accordance with his preceding remarks the addition compound formation would cause a reduction of the restoring force and consequently a

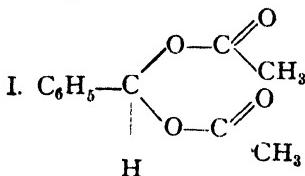
<sup>12</sup> *Rend. R. Acc. Sci. Napoli*, s. iii., **32**, 70, 1926.

<sup>13</sup> *Gazz. Chim. It.*, **46**, 36, 1916.

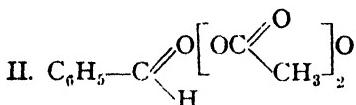
modification of the characteristic frequency. Following this hypothesis and according to the theory of Lewis-Perrin-Trautz, the action of the catalyst would be very clear—it would correspond to the shift of the characteristic frequency from the regions of high frequency towards higher wave-lengths.

He did not seek to find out what could now be substituted for this mechanism.

**Professor Böeseken** (*Delft*) replying to Professor Giordani's remarks concerning the formation of intermediate products during the Perkin reaction, agreed that



I.  $\text{C}_6\text{H}_5-\overset{\text{O}}{\underset{\text{CH}_3}{\text{C}}}(\text{O}-\text{C}_6\text{H}_5)-\text{CH}_3$  was stable and that its formation inhibited the reaction.



II.  $\text{C}_6\text{H}_5-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}(\text{OC}(\text{CH}_3)_2)-\text{O}$  was the first addition compound and

might be an intermediate product necessary for starting the reaction. He distinguished, however, between physical and chemical catalysis as two different ways along which a catalytic reaction might proceed but, in his view, the elucidation of catalytic action should be sought in the physical phenomena alone. In the case of physical catalysis a bimolecular reaction was in reality termolecular; the two molecules must collide at the same moment with the catalyst and at that moment the energy and the entropy (particularly the latter) were changed. When one was dealing with chemical catalysis, in which the action of the catalyst was more or less inhibited, an acceleration of the reaction velocity could never be understood without considering the entropy factors in the compound.

He entirely agreed with Professor Giordani in his remarks on the significance of the *A*-term in the Arrhenius equation, but he presumed that in the formulæ of Scheffer-Kohnstamm the change of the *A*-term by a catalyst was given in a more general form (see p. 618), for not only was the energy-increment changed but also the entropy-increment.

Professor Polanyi in dealing with the keto-enol-equilibrium, had said that a catalyst such as pyridine caused change of the distance between H and O in the mol which according to the wave mechanics theory could be formulated:

$$k = avl \frac{-Q}{RT}.$$

Professor Böeseken remarked that this was a special case of the general formula of Scheffer-Kohnstamm in the integrated form.

In a differentiated form:

$$\ln k = - \frac{\epsilon_i - \epsilon_m}{RT} + \frac{\eta_i - \eta_m}{R} + C$$

the entropy term included the steric conditions of the molecules, e.g., the mutual distances of the atoms in the molecules. With regard to the significance ascribed by Professor Kendall to the addition compounds of HCl with the different substances playing a rôle during esterification and saponification, Professor Böeseken remarked that

G. Baume and G. Pamfil<sup>14</sup> had found that methyl alcohol, propionic acid, and propionic acid methyl esters all formed addition compounds with HCl, but that those compounds, according to the solidification curves, are dissociated to a large extent at temperatures far below 0° C. This decomposition would increase with rise of temperature; if the formation of these intermediate compounds should be a necessary condition for this catalysis, one would expect a negative (or at least an abnormally low positive) temperature-coefficient and this being certainly not the case, the formation of these compounds could never give a satisfactory explanation of the catalytic action.

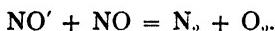
**Professor v. Euler** (*Stockholm*), referring to Professor Giordani's statement, mentioned some previous attempts to calculate the coefficient  $Q$  of the temperature formula

$$k_2 = k_1 e^{\frac{Q(T - T')}{R \cdot T \cdot T'}}.$$

In the case of mutarotation and of catalysed hydrolyses where the heat of the electrolytic dissociation of the substrate could be measured, the coefficient  $Q$  seemed to be determined by the electrolytic dissociation heat of the substrate  $Q_1$  and the ionisation heat of the water. He had mentioned the possibility of such a calculation as long ago as 1899.<sup>15</sup> Concerning mutarotation a more accurate comparison was made with Rudberg<sup>16</sup> and with Ölander.<sup>17</sup>

**Dr. J. Y. Macdonald** said that one point in the scheme proposed by Norrish and Smith to explain their results seemed open to the following criticism.

In the second of the alternative mechanisms suggested to account for the formation of nitrosyl cyanide, the first steps consisted in the activation of nitrogen peroxide and the transfer of this activation to a nitric oxide molecule. Now pure nitric oxide was known to decompose in light of wave-length less than 2000 Å, and the most obvious explanation of this process was represented by the equation:—



There was no evidence whatever of autocatalysis in this reaction, although nitrogen peroxide was formed in considerable quantity. In order to reconcile Norrish and Smith's equation with this fact, it was necessary to assume that nitrogen peroxide could only act as carrier for the lesser amount of energy involved in the combination with cyanogen. Though there was nothing intrinsically impossible in this, it introduced a new conception which seemed unnecessary in view of the alternative mechanism provided.

Norrish and Smith's theory that nitrosyl cyanide was formed as an intermediate product could be tested very directly. According to equation VI., this compound reacted slowly with nitric oxide in the dark, giving nitrogen peroxide, nitrogen and cyanogen. Analyses of the gas mixture immediately after illumination and again after standing overnight should prove beyond doubt whether the equation was valid or not.

Records of the fall of pressure with time in the dark reaction under various conditions should also prove of value.

<sup>14</sup> *Compt. rend.*, **155**, 426-30, 1912.

<sup>15</sup> *Ofversikt Sv. Vet. Akad. Forhandl.*, **4**, and *Z. physikal. Chem.*, **36**, 644, 1901 and

<sup>47</sup>, 353, 1904.

<sup>16</sup> *Z. Physik*, **16**, 54, 1923.

<sup>17</sup> *Z. anorgan. Chem.*, **156**, 143, 1926.

**Dr. R. G. W. Norrish** suggested, with reference to the remarks of Dr. Macdonald, that there was no reason why the photosensitive activation of nitric oxide by nitrogen peroxide should not be regarded as specific. There seemed to be no strong argument for supposing that nitric oxide activated in this way should necessarily react with molecules of its own kind, even though it reacted with cyanogen. However, one might perhaps for the reason he had given prefer the alternative mechanism (*a*) in the paper. With regard to his other points Dr. Norrish quite agreed that experiments on the lines suggested might lead to interesting results, and he hoped that they might shortly be followed up. Their chief difficulty was the great length of time required for separate experiments.

### PART III. NEUTRAL SALT AND ACTIVITY EFFECTS.

**Professor A. Lapworth** (*communicated*) said that organic chemists could not fail to recognise the great advances in the knowledge of homogeneous catalysis in solutions due to Dr. Brönsted's insight and exact experimental work. In his paper on "The Theory of Acid and Basic Catalysts," however, he attempted briefly to appraise the work and ideas of others, including himself (Professor Lapworth) to whose theory of acid catalysis he did something more and at the same time something less than full justice.

As mentioned in the paper (p. 2203) to which Dr. Brönsted referred, Thomsen, Lothar, Meyer, and Lowry, among others, had previously had reason to suppose that the hydrogen ion of aqueous solutions was hydrated.

Dr. Brönsted, like nearly all writers who had discussed Lapworth's theory of acid catalysis,<sup>1</sup> wholly disregarded Part II., which immediately followed Part I. (p. 2200) in which it was shown that the theory proposed did not require that any *free* hydrogen ions should be present. The following quotation from the first page of Part II. conveyed Lapworth's theory in the simplest possible terms:—

" . . . the properties of acids when dissolved in solvents containing bases may merely depend on (1) the extent to which they combine with the bases present, (2) the manner in which they are partitioned between the bases, and (3) the degree to which the resulting salts are dissociated." (The latter expression was used throughout the paper in the sense of "ionised.")

Another quotation from the same page was: "As there is no reason for supposing that hydrogen ions exist in any but infinitesimal concentration, etc." and another from the last page: "The relations given in Part. II. of this paper will be true in practice whether the reality or otherwise of free hydrogen ions is assumed." If these expressions of view were not enough, the penultimate paragraph of the paper (p. 2203) should have made it clear that the writer regarded the idea of reduction in concentration of free hydrogen ions as "*more hypothetical*" than the diminishment of the availability of the acid for salt formation.

It should be added that the relations developed had reference to solutions of acids in any solvent, not only in water. Their accuracy was limited to the range in which the law of mass action was strictly applicable—in other words to "ideal" solutions, containing only such salts as obey the Ostwald dilution law. They could immediately be adapted for salts which were wholly ionised by assigning the value "infinity" to K, the symbol for the ionisation

<sup>1</sup> *J. Chem. Soc.*, 93, 2187 (1908).

## GENERAL DISCUSSION

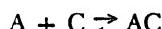
constants of salts, and in the expression given at the head of p. 2202 there was actually shown one result of such a transformation.

**Dr. E. E. Walker** said that in discussing "salt effects" scarcely anything had been said by authors of papers about the effects produced by solutes other than electrolytes. Non-electrolytes also affected the velocity of reaction and the effect might be equal in sign or opposite in sign to that produced by neutral salts.

Solutes in general affected the equilibrium point in balanced actions; catalysts such as acids and bases formed no exception to this rule. That solutes should do so followed logically from the fact that the solvent exerted an influence on the equilibrium point.

About fifteen years ago Professor Armstrong and the speaker studied the effect of solutes on the equilibrium between  $\alpha$  and  $\beta$  fructose. They found that some solutes, such as monohydric alcohols, nitriles, esters, ketones and ethers, displaced the equilibrium in one direction while others such as salts, sugars, polyhydric alcohols, phenolic compounds, urea and thiourea displaced it in the other direction. Similar relationships between the effects of these two groups of substances on the velocity of the hydrolysis of cane sugar were pointed out. The one group accelerated hydrolysis whilst the other retarded it.<sup>2</sup>

Since solutes could affect the equilibrium point of a balanced action, they could affect the velocity of reaction in at least two ways. Take the case of a simple conversion of one substance A into another B in the presence of a catalyst C. Firstly the equilibrium point between A and B might be shifted in one direction or another whereby one or both of the velocity constants concerned must be affected. Secondly the hypothetical but generally accepted equilibrium:—



might be shifted, whereby the concentration of the substance AC (which was the substance undergoing change) was altered. Further light might be thrown on these phenomena by studying the effect of solutes (and perhaps also of solvents) on both the equilibrium point and reaction velocities of suitable reactions.

Much would be gained by dropping the term "salt effect" and adopting the term "solute effect" in its place.

**Professor McBain** (*Stanford, U.S.A.*) said that although the theory of the dissociation of electrolytes lay outside the scope of the present Discussion, it was impossible to elucidate the mechanism of catalysis by electrolytes without being sure of what molecular and ionic species were actually present. For this reason he called attention to experimental data presented in a paper in collaboration with Mr. van Rysselberge which would appear in the current (October or November) number of the *Journal of the American Chemical Society*.

When to a 0.05 molar solution containing a divalent ion a sufficient quantity of common anion was added, the divalent ion formed a complex anion, and one had the striking and highly significant result that the usual movement of the cation of the 0.05 molar salt was suppressed or even reversed. Thus when an excess of sulphate ion was added to a 0.05 molar solution of magnesium or cadmium sulphate the magnesium or cadmium migrated toward the anode. The data showed that all divalent ions, even the simplest, such as magnesium ion and sulphate ion could form complex

<sup>2</sup> *Proc. Roy. Soc., A* 87, 539-554, and *A* 88, 246-252.

anions in such appreciable amount that the ordinary migration of the cation was completely submerged. Such facts appeared to constitute a disproof of the applicability of any hypothesis of complete dissociation to solutions containing divalent ions.

The divalent ion differed only in degree. Thus in a 0·05 molar solution of magnesium chloride to which sufficient concentration of chlorine ion had been added, the magnesium went to the anode just as did cadmium in the presence of potassium iodide, and presumably for the same reason. Proof of the existence of complex ions led almost inevitably to recognition of the existence of undissociated molecules likewise. Examination of the data showed that the formation of complex anions was not confined to high concentrations (such as were dealt with in at least one of the papers presented in this Discussion), but that they were still not negligible in moderate dilution.

Finally, it should be pointed out that the migration data could not be explained in terms of free ions clustered together under the influence of purely electrostatic forces, but that, as shown in the original paper, it was necessary to recognise the molecules and complex ions really present in the solution of these strong electrolytes.

**Professor Giordani** (*Naples*) said that he had heard with great interest the communication of Professor Brönsted, but he would emphasise that the close agreement found between experimental values and the formula (6)

$$k_A = G_1 K_A^x$$

did not support the theory put forward.

In fact Professor Brönsted supposed that the catalytic constant  $k_A$  was related to the kinetic constant of dissociation  $k_{\text{diss}}$ .

Then, since  $k_{\text{diss}} = K_A k_{\text{ass}}$  and further, according to Arrhenius' formula  $k_{\text{ass}} = Be^{-\frac{A}{RT}}$  it followed that  $k_{\text{diss}} = Be^{-\frac{A}{RT}} K_A$ .

By comparison with formula (6), one found,

$$G = Be^{-\frac{A}{RT}}$$

In other words  $G$  ought to be a coefficient variable with the nature of the acid and not a constant. Furthermore  $K_A$  must have always the same exponent (equal to unity in case of direct proportionality between  $k_A$  and  $k_{\text{diss}}$ ). As a matter of fact the experimental values of Professor Brönsted completely fitted his formula when  $G$  was throughly constant and  $x$  varied from 0·2 to 0·8.

It would be preferable to say, in the actual state of affairs, that formulæ (6) and (7) are simply empirical formulas, whose interpretation was still lacking.

**Professor Dawson** referring to Professor Brönsted's communication, said :—

(a) Professor Brönsted's assertion that "the dual theory was established on the basis of a misinterpretation of the underlying facts" could not be accepted. In the first place, the observations of Arrhenius, to which Brönsted referred, had no bearing whatever on the origin of the dual theory. The latter was brought forward to explain the relations which held between the velocities which were observed (a) when the concentration of the catalysing acid was varied, and (b) when the corresponding salt was added to a solution containing a fixed concentration of the catalysing acid. The fact that two such series of experiments led to the same value for the catalytic

## GENERAL DISCUSSION

activity of undissociated acetic acid in the acetone-iodine reaction, indicated that, in that case, salt effects had no appreciable influence on the determination of the magnitude of the quantity  $k_m$  which might be said to have constituted the central feature of the dual theory. From every point of view, the dual theory was entitled to be considered as a clearly defined stage in the transition from the classical theory, which attributed characteristic catalytic qualities to the hydrogen and hydroxyl ions, to the modern view which ascribed catalytic activity to all proton donators and acceptors independently of their electrically neutral or ionic nature.

(b) Two kinds of "salt effects" had been distinguished by Brönsted and by the speaker. In the case of a reaction which was catalysed by the acid HA, the equation for the reaction velocity might be written

$$v = k_h[H^+] + k_a[A^-] + k_m[HA]$$

and the addition of the corresponding salt or of a catalytically inert salt produced two different effects represented respectively by (i) changes in  $k_h$ ,  $k_a$ , and  $k_m$ , and (ii) changes in  $[H^+]$ ,  $[A^-]$ , and  $[HA]$ . Since the velocity was represented as the sum of the products of corresponding terms, it would seem inappropriate to describe (i) as primary, and (ii) as secondary effects. In principle they were of equal importance and in practice it might be that the secondary effects were much greater than the primary effects.

In accordance with his "intermediate complex" theory, Brönsted supposed that the "primary kinetic salt effect" in the reaction  $A + B \rightarrow X$  was measured by the value of  $f_A \cdot f_B / f_X$  to which a definite value might be assigned if the nature of the reacting entities and the ionic strength of the reaction medium was known. There was a certain amount of evidence to support this view, but there were equally potent facts which were at variance with the assumption. Since these could not be adequately discussed at the meeting, it must suffice to record the opinion that neither the primary nor the secondary effects could be expressed in terms of general activity coefficients.

(c) In reference to the suggested extension of catalytic observations to non-aqueous solutions of non-basic character it might be pointed out that such observations had already been made. The study of the auto-catalysed reaction between iodine and acetone in carbon tetrachloride, benzene, and nitrobenzene solutions,<sup>3</sup> had shown that the reaction velocity in these solutions was enormous compared with the velocity in aqueous solutions. It did not seem possible to interpret these observations except by the assumption that the unionised hydriodic acid was an extremely powerful catalyst.

Professor Dawson said in commenting on Professor Goldschmidt's paper that the latter's early work on esterification contributed very largely to the acceptance of the view that catalytic activity must be ascribed to the unionised portion of the catalysing acid. It was not surprising that he found difficulties in co-ordinating the whole of his observations in terms of the dual theory, for this took no account of the catalytic activity of the anion of the catalysing acid. This omission became increasingly important as the ionisation constant of the catalysing acid diminished.

In alcoholic solution, picric acid was a strong acid whilst trichlorobutyric was very weak. The catalytic activity of the picric anion was probably extremely small, whilst that of the trichlorobutyric anion might be very ap-

<sup>3</sup> Dawson and Leslie, *J. Chem. Soc.*, 1909, 95, 1860.

preciable. It was probable that this difference was largely responsible for the observed difference in the behaviour of the two acids when these were used as catalysts in esterification processes.

**Professor Lowry** said that he had first become interested in the problem of homogeneous catalysis when working as an organic chemist on the isomerism of the  $\alpha$ -derivatives of camphor; the discovery of the mutarotation of nitrocamphor had been made with non-aqueous solvents, and under conditions in which the ordinary methods used in studying aqueous solutions could not be applied. It was a matter of special satisfaction that, in spite of the wide difference in the points of view from which the problem had been approached, the final conclusions of Professor Brönsted and himself were in such close accord.

To one who was still interested in organic chemistry, it was remarkable how little reference had been made in the present discussion to the changes of structure which the catalyst is required to bring about; and, in view of the impregnable character of the spectroscopic evidence for the electronic structure of matter, it was equally surprising that no reference had been made to the electrical nature of the processes of chemical change—apart from his own brief reference to the electrolytic theory of catalysis, which he hoped to discuss more fully in a communication to the forthcoming Conference in Paris. It was, however, not sufficient to think of the organic substance, merely as a “substrate,” which underwent some unspecified transformation, since the nature of the catalyst must be adapted to the transformation that it was required to effect. In particular, whilst a mere shock, such as a bombardment by  $\alpha$ -particles, might suffice to smash a molecule into unspecified fragments, the migration of radicles, and the concurrent readjustment of valency electrons in an isomeric change, generally called for a much more delicate mechanism, and for the construction of a more complex system than that provided by a mere binary collision. It was indeed important to distinguish between merely destructive actions, such as the thermal or photochemical decomposition of acetone, which could not be expressed by one simple equation, and an orderly molecular transformation, such as its enolisation and subsequent iodination. The former changes could be discussed effectively with the help of considerations based on the kinetic theory of gases, and on the energy content of activated molecules, whilst the latter could be studied most effectively with the help of theories of ionisation and of electrolysis. The reality of this distinction was shown by the dual character of the present discussion, e.g., in the wide contrast which existed between the points of view from which the decomposition of nitrogen pentoxide and the mutarotation of glucose had been studied and discussed. A similar contrast was seen in Hinshelwood's conclusion from the study of *gaseous reactions* that moisture is only required to initiate explosion, and that there was no known case of a reaction proceeding with a controllable velocity which can be arrested by Baker's method of intensive drying and purification. No similar statement could possibly be made in reference to *reactions in solution*, since the attempt to arrest chemical change by careful purification had been most successful in the tranquil process of mutarotation, and in keto-enolic transformations which could not be conceived as proceeding with explosive violence.

**Mr. W. F. K. Wynne-Jones** (*communicated after the meeting*) wrote that in his treatment of salt effects in reaction kinetics, and more particularly the indirect effect that a salt exerted by altering the concentration of the reacting substances, Professor Dawson had failed to give a complete statement of the problem. Firstly, it might be noted that the main effect

in very dilute solution was due to alteration in the activity coefficients of the ions in accordance with the well-known equation

$$-\ln f = Ac^x \dots \dots \dots \quad (1)$$

Professor Dawson, on the other hand, seemed to regard the effect in dilute solution as due mainly to changes in the activity coefficients of the neutral molecules. Such effects, however, were small and in dilute solution should be linear functions of the salt concentration, whereas there was conclusive evidence that the dissociation of a weak electrolyte varied most rapidly in dilute solution and was represented by an equation of the same type as equation (1).

Secondly, it was evident that Professor Dawson considered justifiable a linear extrapolation of his data to zero salt concentration. Since this procedure caused doubt to be thrown on the validity of his general conclusions it was of interest to indicate a more correct method of treating the results. If the observed velocity of a reaction might be represented by the equation

$$v_{\text{obs}} = v_w + k_H \cdot c_H + k_{in} c_{in} + k_A \cdot c_A \dots \dots \quad (2)$$

where  $v_w$  was the velocity due to the water molecules,  $k_H$ ,  $k_{in}$ , and  $k_A$  were the velocity coefficients of the oxonium ion, the undissociated acid molecules and the anions respectively and  $c_H$ ,  $c_{in}$ ,  $c_A$  were the corresponding concentrations, then by keeping the salt concentration constant and varying the acid concentration one could obtain results which when plotted against the acid concentration would yield a straight line whose intercept on the velocity ions corresponded to the sum of the effects of the water molecules and the anions. By making similar measurements at different salt concentrations the value of " $k_A$ " might be derived and hence the value of " $v_w$ ".

**Professor Dawson** (*communicated later*) said that Mr. Wynne-Jones seemed to imply that the writer had ignored the indirect catalytic effects which were associated with the presence of salts in the reaction medium. This was hardly consistent with the fact that two papers by Dawson and Key<sup>4</sup> had been entirely devoted to the consideration of such indirect effects under the name of "inert salt" effects. These "inert salt," or more generally, "medium" effects, which might be due to changes in the catalytic coefficients or to changes in the concentrations of the active entities, represented variations in the effects produced by pre-existing catalysts. They were appropriately described as "inert salt" effects on the ground that the addition of such salts did not give rise to any effect which demanded the recognition of a new or apparently new catalytic entity.

Since the kinetic problem they had envisaged included the consideration of salt solutions ranging from pure water to the fused salt, it would seem that Mr. Wynne-Jones' reference to the limiting formula  $-\ln f = Ac^x$  was somewhat beside the mark. Finally, in so far as they had employed extrapolation methods for the derivation of catalytic coefficients or for the determination of reaction velocities in salt-free solutions, it would not be difficult to justify the procedure in the particular circumstances which were involved.

**Professor Brönsted** in reply to Professor Giordani said that he did not agree with the conclusion that the coefficient  $G$  in the catalytic equation ought to vary with the nature of the acid catalyst. On the other hand, it was quite right, as he had pointed out, that the mechanism of acid and basic catalysis suggested called for a constant value of  $x$  in the equation  $k = G \cdot K^x$ .

<sup>4</sup> *J. Chem. Soc.*, 1928, 1239, 1248.

passing from one reaction to another. This very simple state of affairs was not the one found experimentally; the  $x$ -values in the various reactions, that is the slope of the straight lines of the logarithmic plots, depended upon the reaction and varied from 0·8 in the basic catalysis of nitramide to 0·4 in the basic catalysis of glucose. This meant that the mechanism of the reactions had not yet been fully elucidated. On the other hand the existence of a definite  $x$  value pertaining to each catalysed reaction was a fact of very considerable interest, and it was to be expected that the insight obtained by further investigation in this field would contribute considerably to throw light upon the nature of homogeneous catalysis.

In reply to the remarks of Professor McBain he said the modern theory of ionic interaction did not dogmatically ascribe 100 per cent. dissociation to all salt solutions. In concentrated solutions, and particularly when multivalent ions were present undissociated salt-molecules of polar nature certainly do exist. However transference experiments in mixed salt solutions were not particularly suitable for the investigation of this question.<sup>5</sup> Electrometric experiments by the speaker<sup>6</sup> had shown that undissociated molecules like  $MgCl_2$  were not present even in a strong  $MgSO_4$  solution.

Professor Lowry's point of view, that acid or basic catalysis was always a combined effect of acids and bases was explicable as a result of his own interesting observations in the field of prototropic changes. In the work of Bronsted and Guggenheim the same idea was adopted to explain the phenomena of mutarotation and provided admittedly a very simple interpretation of the catalytic mechanism. It should, however, not be overlooked that only a fractions of catalytic reactions were accelerated by both acids and bases. Acid and basic catalysis should be recognised as being frequently separate effects, even though a mechanism as simple as in the case of prototropic changes could not be found. The question of the mechanism, on the whole, seemed to the speaker for the present moment to be of minor importance as compared with that of the laws by which the phenomenon of catalysis was governed. For a long time the contribution to the discussion of catalysis had mainly consisted in advancing various possible explanations of catalytic mechanism, each as unfounded and arbitrary as the other. The time had now arrived to provide such experimental evidence that a comprehensive and conclusive description of the phenomena could be obtained.

In this respect the extended theory of acid and basic catalysis now put forward seemed a step forward. It was important and promising that this theory had now support from various quarters. For a sound development of the theory it was necessary however to adequately consider kinetic salt effects. When Professor Lowry in his introductory address spoke about a "complete repudiation of the theory of Arrhenius and Ostwald" by the fact that salts such as sodium acetate possess a direct basic catalytic effect, he (Professor Bronsted) did not agree with him. In the case of cane sugar inversion referred to, the effect of added sodium chloride was no such direct acid catalysis, but a *primary salt effect* interpretable as a medium effect which was by no means contradictory to the assumption of the hydrogen ion being in this case the only catalytically active molecule. In fact, in view of the change which, in other respects, was caused in the medium when its nature was altered from a zero to a 0·4 normal sodium chloride solution, it would be remarkable, and would call for a special explanation, if the medium proved kinetically constant under such conditions.

<sup>5</sup> Cf. Bjerrum and Ebert, *Kgl. Danske Vid. Selsk. Medd.*, 6, No. 9 (1925).

<sup>6</sup> Brønsted, *ibid.*, 3, No. 9 (1920).

A similar lack of appreciation of the kinetic salt effect characterised the communication of Professor Dawson, although he also was a strong supporter of the views contained in the theory put forward. When Professor Dawson spoke about "inert salt" effect and the insignificance of the "Arrhenius observation" for the development of the dual theory, he did not seem to realise that the same effect was caused also by salts which possessed direct catalytic properties by virtue of their ions being acids or bases. In other words, the presence of a direct catalytic effect of the ions did not exempt them from exerting the ordinary electrostatic effect. When diluting an acetic acid—acetate buffer, the ratio acid/base being unchanged, the solution would not remain "isohydric" in the classical sense of this word (in the modern sense the word "isohydric" had not been defined). The change in the hydrogen ion concentration on such dilution was a *secondary salt effect* which of course must be considered in all cases when the hydrogen ion contributes measurably to the velocity. That in some cases of catalysis there was no salt effect was a different matter. The primary salt effect might incidentally be zero or small in the dilute range, depending upon the reaction; the secondary salt effect might be zero or small in the dilute range, depending upon the buffer. This was a matter to be decided separately from the general viewpoint of the theory of kinetic salt effect in each individual case.

Observations in the nitramide catalysis might be quoted to show this diversified behaviour. Whilst in an acetic acid—acetate buffer the salt effect under ordinary conditions was negligible in dilute solution, the catalysis by 0·1 normal free acetic acid was increased by 20 per cent. on addition of 0·1 normal NaCl owing to the increase in dissociation of the acid (secondary salt effect); a still more marked increase by addition of salts took place when an acetic acid-hydrochloric acid buffer was used in which the concentration of the catalysing acetate ion was the only one which could be changed by the equilibrium displacement.

At the time of the development of the dual theory very little was known about this kind of phenomena and a sound interpretation thereof was entirely lacking. Now the theory had been advanced and extensively verified, the old data should necessarily be revised and reconsidered in the light of the new ideas.

Professor Dawson had attempted an explanation of the increased dissociation of a weak acid on salt addition by attributing to the acid a polar structure. This explanation, however, could not be accepted because the phenomenon of increased dissociation was already accounted for in an entirely satisfactory manner on the basis of the ionic attraction theory *without* any such assumption as to the nature of the acid molecule. In fact the existence of a dipole structure of their molecule would rather decrease the effect in question, since the activity coefficient of a dipole is influenced by salt addition in a similar way as the activity coefficient of an ion.

In connection with Professor Euler's communication, Professor Brönsted remarked that the explanation of the fact that the glucose mutarotation was catalysed by electrically neutral molecules such as acetic acid or ammonia could hardly be reconciled with the contention of the increased reactivity of ions. If the product of the reaction of glucose with the hydroxyl ion reacted rapidly because it was a charged molecule  $[C_6H_{12}O_6 \cdot OH]^-$  or  $[C_6H_{11}O_6]^-$  there seemed to be no explanation of the reactivity of  $C_6H_{12}O_6 \cdot NH_3$ , the substance which, according to Euler, should be the reacting molecule in the ammonia catalysis of glucose and which bore no

electric charge. Neither could such complexes be classed as compounds of the "type of salts." Recognition of the phenomena underlying the theory put forward, therefore, would seem to necessitate a rather radical modification of the points of view underlying the "ionisation theory" of catalysis.

(Communicated later) : This "ionisation theory" was actually to be classed as a special case of the theory of compound formation in general, which had been particularly advocated by Professor Kendall and seemed to be favoured by many other investigators. He (Professor Brönsted) was unable to visualise the kinetic significance of compound formation as a general explanation of kinetic or catalytic phenomena. Obviously the theory of Kendall did not claim that compound formation should always be accompanied by reactivity, but on the other hand it did not bring forth any reasons why the converse should be true. In many cases the "stability" of the "intermediate product" (as shown for instance by the possibility of its being isolated in a pure state) was taken to greatly favour the idea of its catalytic significance, while from other points of view it ought to be extremely unstable in order to be of any assistance in promoting the reaction. The truth undoubtedly was that the fact of two molecules A and B forming a compound AB in solution did not influence in any general way the possibility of their reacting with one another. If the compound AB were supposed to react unimolecularly, the particular difficulties in the kinetics of this sort of reactions were at once encountered. If AB reacted by meeting another A or B molecule a new compound formation ( $A_2B$  or  $AB_2$ ) should take place in order to explain the reaction, and so on. The compound formation theory, therefore, only accumulated difficulties of its own, without giving any indication as to how other difficulties could be avoided.

The question discussed in Professor Skrabal's communication regarding the significance of the relative velocities with which an intermediate product is formed and decomposed was essentially the same as that discussed by him (Professor Brönsted) in his monograph on acid and basic catalysis. The distinction between "Arrhenius intermediate compounds" and "van't Hoff intermediate compounds" corresponded to the distinction between the "ionisation theory" and the assumption of a direct kinetic action. Also the conclusion that the Lowry mechanism of prototropic change should be described as a "van't Hoff mechanism" was actually necessitated by the results of the suggested catalytic theory as previously pointed out by Brönsted and Guggenheim. The much wider idea that any acid or basic catalysis was describable as a *van't Hoff* mechanism was however a direct transcription of this theory.

**Professor Ch. Moureu (Paris)** said that Professor von Euler's report contained many views of general interest and seemed to him very suggestive. He would consider only two main points, concerning catalytic reactions, as a result of general and personal impression of the discussion.

(i) Professor von Euler said: "The chief problem of chemical kinetics, in my view, is solved when it is possible to calculate in advance the reaction velocity of a catalytic system from the concentrations and from the individual constants of catalyst and substrate."

In general, the experimental verification of theoretical calculation, in catalytical reactions, was possible and relatively easy. But often it was not, and one found, in consecutive trials, more or less divergent, and sometimes very divergent, results. The explanation was very simple; conditions were most of the time not the same, although the experimenter thought that they were the same. The great difficulty of catalytical experiments came from

the great sensitiveness of reactions. A trace of foreign, unknown, substance was often sufficient to overthrow the whole system. They were imponderable impurities: traces of iron, of copper, of alkalies, the alkali coming from vessels; glass could often modify the behaviour of a reaction.

A substance which was always present in all reactions, because it surrounded all existing material objects, was oxygen; oxygen was extremely active and most of the time one neglected its presence and its action. Oxygen was not always an enemy, however, in chemical reactions; very often it was a helping friend, and sometimes even a precious necessary friend. He would recall the case of Sabatier and Senderens' hydrogenation catalysis, in which one of his pupils, M. Mignonac, professor at Strasbourg University, had definitely established the necessity of the presence of a trace of oxygen.

Another omnipresent agent was an immaterial agent, light. How many reactions were catalysed by light; how many parasitical reactions were produced by light, and usually unknown to investigators! This was because light, as everybody knew, afforded at room temperature an energy which could be supplied by heat only at high temperatures—temperatures at which substances, specially organic substances, were destroyed.

(2) In another part of his report, Professor von Euler expressed himself thus: "The problem of catalysis is a chemical one, and naturally we have to look for the relation between the chemical structure of the substrate and its reaction velocity."

The reading of this phrase had caused him very great pleasure. He agreed that catalysis was above all chemistry. Perhaps it would not be without interest to repeat and affirm this sometimes and especially in meetings of physical chemists as important as the present meeting. For, in the end, whatever be the view, from the standpoint of energy, that one considered, one must necessarily arrive at chemistry, which was, let it not be forgotten, the science of transformations of matter.

For that reason he regretted very much that too many physico-chemists, and especially the young ones, at least in his own country, in France, began to study physical chemistry without being previously accustomed to experimental chemical work. As Professor von Euler had very well shown, in establishing in a concrete case, by measurements of the reaction velocity, the existence of intermediate compounds between enzyme and saccharose, and also, as various colleagues (particularly Professor Boeseken and Professor Lowry) had said, intermediate compounds were undoubtedly formed in catalytical reactions. The ideal was to be able to isolate them. Their isolation, however, involved not physics, but chemistry, and even difficult chemistry, on account of the fugitivity of intermediate compounds. To isolate these intermediate compounds one must be a clever chemist.

He could never too much advise young future physical chemists to study and practise chemistry first and as long as possible, and not to be in such a hurry to undertake physico-chemistry, in which study they would spend thereafter their whole life.

He seemed, it was true, to have wandered from the subject treated by Professor von Euler: *compounds between catalysts and substrates and their reactivity*. He had, naturally, not addressed to Professor von Euler the above few reflections; Professor von Euler, in view of all his important works on catalytical reactions (those particularly concerning the very sensitive action of enzymes) appreciated those considerations better than the speaker. He spoke to young physical chemists, and to them he said: "First of all, be good chemists, and particularly, in catalytical researches

beware of the impurities which chemical systems always contain. Always think of two agents everywhere present: oxygen and light."

They would pardon him for giving these hints to the young men, because of his burning enthusiasm for science and his deep sympathy for all the young scientists who would be their successors to-morrow and would bear in their hands the sacred torch, and also because of his already long personal experience.

**Professor Dawson** referring to the paper of Professor Harned and Dr. Åkerlöf said that in renouncing his former view that the phenomena of acid catalysis were to be explained in terms of individual ionic activity coefficients, Professor Harned had taken an inevitable step. His present view suggested some slight advance towards a more rational interpretation of the facts, but so long as formal and general thermodynamic coefficients were supposed to determine the nature and magnitude of salt effects, it was tolerably certain that no consistent interpretation of such effects would be possible. The catalysed reactions referred to by Harned and Åkerlöf were admitted by the authors to show no evidence of that uniformity which would be expected on the basis of their own views.

With reference to reactions of the type of ester hydrolysis in which the concentrations of the substrate and of the catalysing acid were constant, it had recently been shown that the reaction velocity might be accurately represented by the very simple equation  $v = k[H^+]$  if the conditions were such that the catalytic effects of other "acids" and "bases" could be neglected in comparison with that due to the "hydrogen" ion. In this equation  $k$  and  $[H^+]$  depended upon the reaction medium. When salt solutions were in question the variations in  $k$  and  $[H^+]$  could not be expressed by coefficients which did not take adequately into account the nature of the constituent ions.

**Professor Lowry** found himself in complete agreement with Professor Rice in his conclusion that "such changes as keto-enol tautomerism, or other changes involving complicated molecules cannot be explained by . . . a collision hypothesis." Professor Rice had, however, been unfortunate in that he had not succeeded in stabilising the materials with which he had worked, since it was difficult to study the influence of an added catalyst in a system which already contained a catalyst of unknown character and concentration. If, however, experiments could only be carried out under these conditions, the ratio of the velocities of the catalysed and uncatalysed actions was probably of less significance than their difference, since Dawson's work had shown that an additive law could be used to express the simultaneous effect of several catalysts on the same reaction. Attention might be directed, however, to the remarkable stability of the ketonic and enolic forms of the  $\alpha$ -diketones, which M. Henri Moureu had isolated by such ingenious and logical methods. The methylated and acetylated sugars had also proved to be very well adapted for experiments in which it was necessary to arrest a chemical change as completely as possible before proceeding to study the effects of adding a trace of a catalyst. Thus it was with this series of compounds that the impotence of pyridine as a catalyst had been established<sup>7</sup> as well as the remarkable potency of dilute acid and alkali, in contrast with the impotence of neutral water.<sup>8</sup>

The approach to the problem of catalysis from the side of organic chemistry, and in particular of isomeric change in non-aqueous solutions, had been of value in the first instance in showing that these changes are

<sup>7</sup> Lowry and Richards, *J. Chem. Soc.*, 127, 1385, 1925.

<sup>8</sup> Lowry and Owen, *Proc. Roy. Soc.*, 1928, 119, 505.

## GENERAL DISCUSSION

not spontaneous; thus it was only when there had been prepared sugars which could be studied in non-aqueous solvents that it was possible to establish the fact that there is no "tautomeric" transformation, apart from interaction with a solvent of a well-defined chemical type. A second result of working in this field was that, at a time when all other workers were talking of catalysis by bases as if this were an exclusive property of "hydroxyl ions" and were actually using this property to measure the concentration of these ions, the possibility of catalysis by nitrogenous bases in non-aqueous media had already been established<sup>9</sup> and moreover these bases had been shown to be of amazing potency under conditions which excluded any appreciable development of hydroxyl ions. Finally, it was by working with a methylated sugar and in non-aqueous media that in opposition to the earlier observations of all other workers, the impotence of pyridine and of cresol as catalysts was established, as well as their great potency when mixed to form an amphoteric solvent.<sup>10</sup>

The theory that an acid and a base are both needed in order to bring about the migration of a proton in a prototropic change was, of course, limited by the possibility of autocatalysis, when the substance catalysed is itself definitely acid or basic. Thus nitrocamphor was such a strong acid that the addition of another acid in order to convert a base such as piperidine into a complete catalyst appeared to be unnecessary. This was also the answer to the point raised by M. Henri Moureu, in reference to the possible formation of salts on adding a nitrogenous base to an  $\alpha$ -diketone, since the formation of such a salt would bring the  $\alpha$ -diketones into the same class of autocatalytic compounds, requiring only a base in order to provide a complete catalyst.

In conclusion, the challenge in which this general discussion had its origin might be repeated. Was there anyone who still believed that hydrogen and hydroxyl ions were the only real catalysts when catalysis is effected by acids and bases? or that the observations made in Copenhagen and in Cambridge, as well as at Leeds, on the catalytic activity of other ions (such as  $\text{NH}_4^+$  and  $\text{CH}_3\cdot\text{CO}\cdot\bar{\text{O}}$ ) and of neutral molecules (such as  $\text{NH}_3$  and  $\text{CH}_3\cdot\text{CO}\cdot\text{OH}$ ) could be explained away as secondary effects produced by an increased activation of the hydrogen and hydroxyl ions in the solution? When first made, these observations were so difficult to explain that they seemed almost irrational. The modern definitions of acids and bases, as donors and acceptors of protons, which were advanced almost simultaneously by Professor Brönsted<sup>11</sup> and by the author<sup>12</sup> in 1923, together with the experimental evidence that the catalytically active ions and molecules could all be included in the scope of these definitions, had, however, provided a logical solution of this problem. It was, therefore, now only necessary to get rid of the purely hypothetical terms "hydrogen ion catalysis" and "hydroxyl ion catalysis," and to revert once more to the simpler terms "acid catalysis" and "basic catalysis," which alone had any trustworthy experimental significance.

**Professor Farrington Daniels** (*Wisconsin*) said, with regard to Professor Rice's communication, that nitrogen pentoxide, when dissolved in carbon disulphide, decomposed about three times as rapidly as in the normal conditions in a vacuum and that in nitromethane the decomposi-

<sup>9</sup> Lowry and Magson, *J. Chem. Soc.*, 1908, 93, 107.

<sup>10</sup> Lowry and Faulkner, *J. Chem. Soc.*, 1925, 127, 2883.

<sup>11</sup> Rec. Trav. Chim., 1923, 42, 718.

<sup>12</sup> Chem. and Ind., 1923, 43, 43.

tion was about two-thirds the normal rate. In carbon tetrachloride and in chloroform the rates were slightly faster than normal.

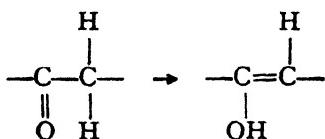
It seemed to be fully established that the nitrogen pentoxide decomposition was unimolecular at the higher concentrations, and the best explanation at present was based on molecular collisions combined with an internal complexity of the molecule. Under these conditions the influence of a solvent in affecting the reaction rate was a matter of great importance. In the gas phase, carbon disulphide vapour accelerated the decomposition, possibly by forming an intermediate compound of still greater complexity and with more degrees of freedom. Such a complex molecule might decompose at a faster rate. The retarding effect of the nitromethane had not been satisfactorily explained as yet.

**Professor Giordani** in reply to Dr. Daniels, expressed the opinion that the negative influence exerted by nitromethane in the decomposition of  $N_2O_5$ , as well as similar facts, could be easily interpreted by the addition compound theory.

He asked Professor Polanyi whether, in his calculations, the value of  $\nu$  was equal to  $\frac{Q}{h}$ ,  $h$  being Planck constant. If that were so, the empirical formula of Dushmann would receive a sound theoretical basis.

**Professor Polanyi (Berlin)**, said that the coincidence of the reaction velocity of the decomposition of  $N_2O_5$ , as well as of the racemisation of pinene in the gas phase and in solutions, had been pointed out by Professor Rice, and the question of the nature of the internal process which led to this constancy in the rate of chemical change had been raised by Professor Rice and by other contributors to the Discussion. It had been remarked, that as yet no conception had been put forward as to the mechanism of chemical reactions going on in the interior of a molecule.

In a paper then in course of publication,<sup>13</sup> E. Wigner and the speaker gave the following explanation of the intramolecular mechanism : Let there be taken for example a keto-form passing over to an enol-form



They imagined that the H-atom could be pulled out of its normal equilibrium position into a state of unstable equilibrium on the top-level of the elevation of potential energy that separated its ketonic and enolic positions. To determine the rate of transformation, one had to calculate the probability of such an extrusion of the H-atom taking place by a chance accumulation of the intramolecular energy caused by its spontaneous fluctuation in the interior of the molecule.

The way to calculate this was briefly the following : assuming that the H-atom had been pulled out into the intermediate position described above and had then been let loose, it relapsed into its initial position and the energy would dissipate throughout the molecule. The object was to determine the probability of the reverse process of this dissipation.

Calculation of the elastic dissipation of the vibration energy liberated at the letting loose of the H' atom showed that this process was practically

finished in a time of the order of magnitude  $\frac{1}{v}$ ,  $v$  being the atomic frequency. The probability of the occurrence of a spontaneous process was equal to

$$\frac{\text{statistical probability}}{\text{life period}}$$

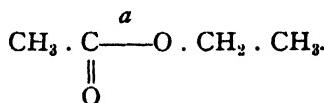
The statistical probability of the extruded state was  $e^{-\frac{Q}{RT}}$ , and hence reaction velocity was equal to

$$\frac{e^{-\frac{Q}{RT}}}{\frac{1}{v}} = ve^{-\frac{Q}{RT}}.$$

This explained why the factor  $A$  of the Arrhenius equation  $Ae^{-\frac{Q}{RT}}$  was, in monomolecular reactions, generally of the order of magnitude  $10^{14}$ , this being the order of magnitude of the frequency of atomic vibrations. It led also to the suggestion that if solvents and homogeneous catalysts affected the (primary) velocity of monomolecular reactions, they did so only by changing their activation heat.

Professor Polanyi further said, in reply to the question of Professor Giordani, that the value of  $v$  in the formula given by Wigner and himself was not equal to  $\frac{Q}{h}$  but should be about five to ten times smaller. The difference, however, lay within the range of the inexactitude of the factor  $A$  in Arrhenius' formula. Besides it would be shown in the paper dealing with this subject, that often the factor  $A$  would not be equal to  $v$ , but to  $v\sqrt{\frac{Q}{RT}}$  or  $v\frac{Q}{RT}$ , the variation depending on the mechanism of the reaction.

**Professor v. Euler** (*Stockholm*) wished to emphasise his agreement with Professor Polanyi's view, that the *increase of distance* between the groups of the molecule, which are split in a catalysed reaction, was of essential importance, and that the energy of activation of the substrate was—at least in a great part—the distance-energy of the activated molecules. The great instability, *viz.*, the high specific reaction velocity  $rq$  of the interacting ions, compared with the non-dissociated molecules seemed to him to be caused by a low degree of symmetry of the interacting ions, connected with the increased distance,  $a$ , between the groups to be split, *e.g.*, between the acetyl-group and the ethoxyl group of an ester:<sup>14</sup>



**Professor F. O. Rice** (*John Hopkins*) (*communicated later*) referring to Dr. Polyani's remarks said that the velocity measurements made so far were only relative. It was proposed to make velocity determinations with less sensitive keto-enol substances and make absolute velocity measurements, in which case it would be possible to test equations giving relationships between frequency and activation. It might be noted that the heat of activation in the pure liquid state was very large, being almost 50,000 cal. per mol. It might be that this represented the energy required to

<sup>14</sup> H. v. Euler, *Sv. Vet. Akad. Arkiv f. Kemi*, 9, No. 30, 1926.

separate the mobile hydrogen from its carbon atom to such an extent that it could make the jump to the carbonyl oxygen. The energy required to disrupt completely the C—H bond<sup>15</sup> was 90,000 cal.

It would seem unwise to neglect completely considerations of the mechanism of chemical changes ; in the past these had proved very valuable aids in discovering the laws that govern chemical reactions, and there seemed no reason to suppose that investigators no longer required the use of this tool. The work on the rate of change of aceto-acetic ester did not support any mechanism based on hydrogen or hydroxyl ion catalysis, since a minute trace of piperidine or bromine in the pure dry ester accelerated the reaction in remarkable fashion. These results supported the theory of acid and basic catalysis proposed by Professor Brönsted.

**Professor V. Euler** (*communicated later*) remarked that Professor A. Skrabal in his report had stated, concerning Euler's theory : "In order to measure the values  $G$  and  $k_s$  one must use strongly acid or strongly basic solutions and work under quite different conditions of medium content than when ascertaining the value of  $k$ ." This deduction was not in accordance with the results obtained by Euler and Ölander concerning the hydrolysis of dioxopiperazine<sup>16</sup> and on the hydrolysis of succinimide.<sup>17</sup>

**Professor N. R. Dhar** (*communicated later*) said that in two communications<sup>18</sup> he had occasion to investigate the influence of different salts on the velocity of the following reactions at different temperatures :—

- (1) Oxalic acid and chromic acid.
- (2) Formic acid and chromic acid.
- (3) Sodium formate and mercuric chloride.
- (4) Sodium formate and iodine.
- (5) Sodium formate and silver nitrate.

In the above reactions some salts, notably those of potassium, sodium, and ammonium accelerated reaction whilst others, salts of magnesium, calcium, strontium, barium, etc., retarded the chemical change. It was observed that the neutral salt effect did not change with increase in the temperature of the medium. It was quite difficult to give a quantitative explanation of the above facts, but on qualitative lines one could explain them from the point of view of the increase of dielectric constants of the medium on the addition of the first group of salts. It was highly desirable that the problem of "salt action" should not be considered only in regard to the cases of acid or basic catalysis, but should be extended to the investigation of all kinds of chemical changes.

<sup>15</sup> See Bates and Andrews, *Proc. Nat. Acad. Sci.*, **14**, 124 (1928).

<sup>16</sup> *Z. physik. Chem.*, **134**, 381. <sup>17</sup> *Ibid.*, **137**, 393, 1928.

<sup>18</sup> *Annales de Chimie*, 9th series, **130**, 1919; *Zeit. anorg. Chem.*, **128**, 229, 1923.

## CONCLUSION.

BY PROFESSOR T. MARTIN LOWRY.

To summarise a General Discussion is a difficult task, since its fruitfulness depends so largely on personal interactions which are not recorded in the printed report. It must also be confessed that an impartial summary is an ideal which it is almost impossible to attain, when the reporter is himself keenly interested in the subjects under discussion. It is, therefore, perhaps desirable to admit the purely personal character of the impressions recorded below.

Foremost amongst these impressions is the apparently unanimous acceptance of the view, which the discussion was intended to confirm or to destroy, that *catalysis by acids and bases is not limited to hydrogen and hydroxyl ions*. Thus, in direct opposition to the early dictum of Ostwald, it is now admitted that catalytic activity is a general attribute of all ions and molecules possessing acid or basic properties, in the sense of the wider modern definitions, which include under these terms all those ions or molecules which can give or accept a proton. The general acceptance of this fundamental proposition was shown by the fact that criticism was directed almost entirely to the magnitude of the corrections which must be introduced in the catalytic coefficients of the various ions and molecules in order to take account of the effects produced by the presence of salts. The reality of these effects, as well as their secondary character, was shown in the papers contributed to the discussion, but this conclusion is quite different from the claims formerly made by some irresponsible critics, that the catalytic activity of all other components of the solution could be explained away if proper values were assigned to the "activities" of the hydrogen and hydroxyl ions. A much more difficult problem was opened up, however, by Professor Brönsted's attempt to correlate the catalytic coefficients with the dissociation constants of various acids and bases. The relationship between these quantities is at present purely empirical, and no adequate theoretical interpretation of it has yet emerged.

During the course of the meeting, Professor Moureu's explanation of the action of inhibitors in autoxidation was criticised in the hearing of the reporter on the ground that it was based on Berzelian conceptions of chemistry. This criticism might be regarded merely as a tribute to the fact that Professor Moureu has refrained from expressing his views in an ultra-modern phraseology, or it might imply that these views are incompatible with the physical chemistry of the present day. Special interest attaches therefore to a short note (p. 706), sent by Professor Christiansen as a written contribution to the printed discussion, in which the implications of Professor Moureu's equations are analysed in a more detailed way than in Dr. Rideal's paper on "Inhibition." Professor Christiansen concludes that the mechanism proposed is not sufficient to explain the experimental results of Moureu and Dufraisse, since his analysis shows that the velocity of oxidation of A might be increased, but could never be decreased, by the

addition of B. It becomes sufficient, however, as several authors have shown, when some chain-effect is assumed. Such an interpretation, I believe, Professor Moureu would be quite ready to accept.

Professor Boeseken's insistence that catalysis may be effected by a physical process of "dislocation," depending on molecular induction, as well as on a chemical process of compound-formation, attracted well-deserved attention. There is already some evidence, however, that the terms "physical" and "chemical" catalysis may degenerate into convenient but meaningless catchwords. In the same way Professor Christiansen found it necessary to call attention to the risk of trying to classify chain reactions into (1) material or chemical chains (*Stoffketten*), and (2) energy or physical chains (*Energieketten*).

One other primary object of the discussion appears to have been fulfilled, since no attempt was made to dispute the claim that certain monomolecular actions, such as the thermal decomposition of nitric anhydride, acetone or propionaldehyde, can proceed apart from either homogeneous catalysis by water-vapour or heterogeneous catalysis by the walls of the containing vessel. It was indeed suggested that the arrest of chemical change by Bakerian purification and drying is confined to explosive reactions (such as the branched-chain reactions discussed by Semenoff); but this rule can obviously not be made to cover the arrest of mutarotation in non-aqueous solutions.

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*Figures in heavy type against authors' names indicate personal contributions to the Discussion.*

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